Control and Monitoring of Temperature in 3D-Printed Circular Disk Reactors for Continuous Flow Photochemistry using Raspberry Pi Based Software

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Electronic supplementary information (ESI) available

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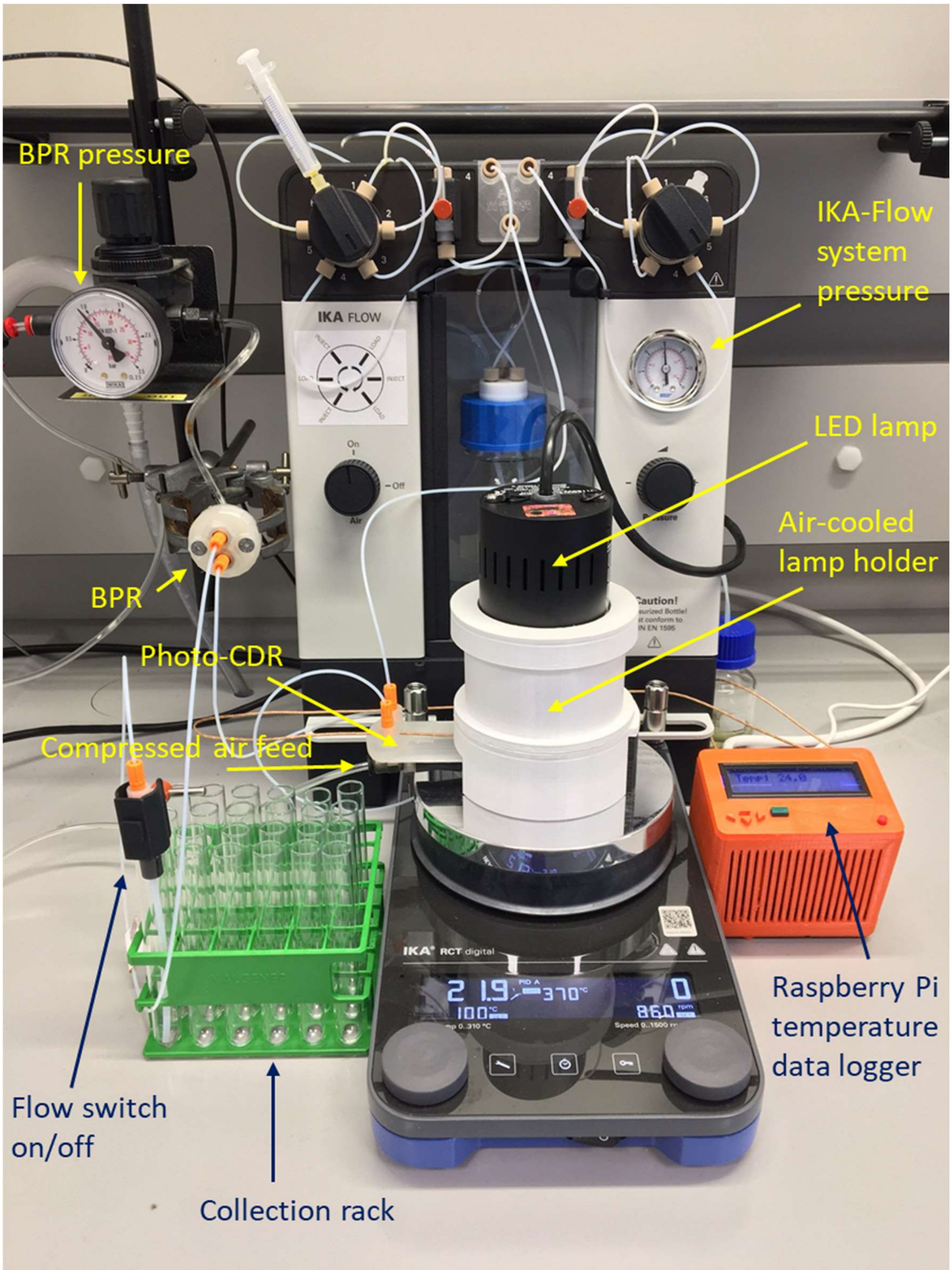
Supplementary Contents

S1. Experimental



Supplementary Figure 1: Experimental setup with compressed air-cooled lamp holder, Kessil H150W 32 W blue 450 nm and Raspberry Pi temperature probe data logger. IKA-Flow system providing the pump and loops for the fluidic system. 3D-printed BPR controlling flow rate

Supplementary Figure 2: Experimental setup with compressed air-cooled lamp holder, Kessil H150W 32 W blue 450 nm and Raspberry Pi temperature probe data logger. IKA-Flow system providing the pump and loops for the fluidic system. Apparatus shown shielded by Asynt safety shield in amber 500 acrylic.

S1.1 General experimental and analysis

All reagents obtained from commercial sources were used without further purification. Anhydrous solvents were obtained from commercial sources and used without further drying.

The reactions were monitored using ^{1}H-NMR and TLC.

Thin layer chromatography was conducted with 5 cm × 10 cm plates coated with Merck Type 60 F254 silica-gel. Analytical shortwave UV (245 nm) or KMnO4 were used to visualise components. ^{1}H NMR data were recorded on a Bruker AV400 spectrometer.

^{1}H-NMR measurements were performed on Bruker Avance III 500 MHz spectrometer, Bruker Avance III 400 MHz spectrometer, Bruker DPX 400 MHz spectrometer and Bruker Avance NEO 400 MHz spectrometer, using DMSO-d6 or CDCl3 as solvent. ^{1}H NMR data is in the form of delta values, given in part per million (ppm), using the residual peak of the solvent (2.50 ppm for DMSO-d6 and 7.26 ppm for CDCl3) as internal standard. ^{1}H, spectral data were visualized and processed using MestReNova software. Chemical shifts are expressed in ppm (δ) relative to the standard and coupling constants (J) in Hz. Splitting patterns are designated as: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet), br s (broad singlet), br d (broad doublet), br t (broad triplet), br m (broad multiplet), dd (doublet of doublets), td (triplet of doublets), dt (doublet of triplets), qd (quartet of doublets), ddd (doublet of doublet of doublets), dm (doublet of multiplets).

Mass spectra (MS) and the retention time (RT, minutes) were run on LC-MS system using the following method and conditions:

Equipment; Agilent 1290 Infinity II series instrument connected to an Agilent TOF 6230 single quadrupole with a ESI source. HRMS were determined on Agilent TOF 6230, ion source temperature 200 °C, ESI +/-, ionization voltage: (+-)4.5 kV.

Column C18, Φ50 x 2.1 mm, 2.5 μm (Phenomenex).

Eluents: A (H_2O + 10 mmol / ammonium formate + 0.08% (v/v) formic acid at pH ca 3.5), B (95% Acetonitrile + 5% A + 0.08% (v/v) formic acid).

Detection: 230 nm, 254 nm and 270 nm.

Gradient: 0.0-0.12 min (A/B = 95/5 flow 1.3 mL/min), 0.12-1.30 min (A/B = 95/5-5/95 flow 1.3 mL /min), 1.30-1.35 min (A/B = 5/95 flow 1.3-1.6 mL/min), 1.35-1.85 min (A/B = 5/95 flow 1.6 mL/min), 1.85-1.90 min (A/B = 5/95 flow 1.6-1.3 mL/min), 1.90-1.95 min (A/B = 5/95-95/5 flow 1.3 mL/min).

Chemical names were generated using ACD/Labs 2019.1.2. (File version: C05H41, Build: 111302, 27 Aug 2019)

S1.2 Material and 3D Printer Settings

Print material was supplied by Ultimaker and is 2.85 mm in diameter and comes on a 500 g spool. Settings were as per the manufacturer's instructions. PLA (2.85 mm filament) was purchased from Ultimaker. All components of the air-cooled lamp holder were printed in PLA. PP – polypropylene (2.85 mm filament) was also purchased from Ultimaker. PP was used to print the photo-CDRs.

3D Printing was carried out on an Ultimaker 3 3D printer or Ultimaker S5 3D printer. Parts in polypropylene were printed on the Ultimaker S5 and the settings used are detailed below.

	Material		
Condition	**Polypropylene**	**PLA**	**PETG**
Settings			
Print core temperature (°C)	240	200	245
Build plate temperature (°C)	85	60	85
Print speed (mm/s)	25	70	60
Fan speed (%)	20	20	20
Print quality			
Layer height (mm)	0.1	0.15	0.15
Wall thickness (mm)	1.14	1	1.3
Top/bottom thickness (mm)	1	1	1.2
Infill density (%)	100	20	20
Infill pattern	Octet	Triangles	Triangles
Build plate adhesion			
Prime blob	Enabled	Enabled	Enabled
Adhesion type	Brim	Brim	Brim
Plate adhesion sheet	PP	None	None

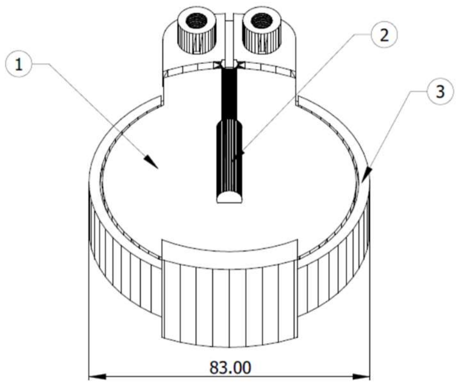
S1.3 STL Files

STL files that can be used to 3D print the air-cooled lamp holder can be found at https://github.com/vernalis/3Dprint_files

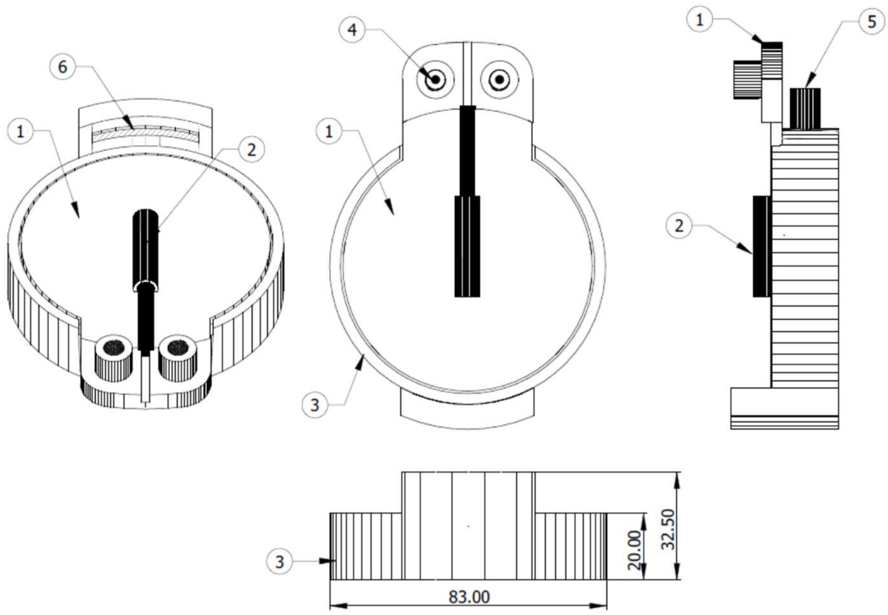
The code for the Raspberry Pi temperature probe data logger used can be found at https://github.com/vernalis/digital-lab

S2. Design of the air-cooled lamp holder

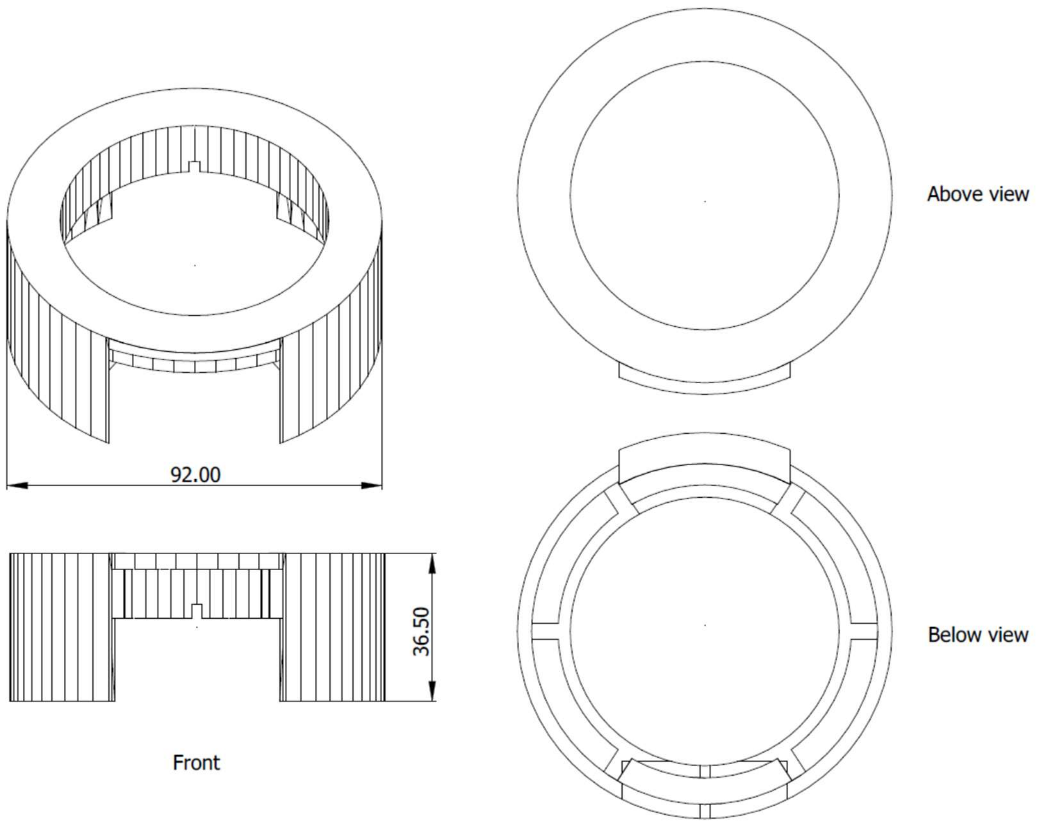
S2.1. Bill of materials



Supplementary Figure 3: TechdrawCAD design file showing projection of air-cooled Photo-CDR base with Photo-CDR in position. (1) Photo-CDR, (2) recess for housing a temperature probe in the Photo-CDR, (3) air-cooled base.



Supplementary Figure 4: TechdrawCAD file showing plan of assembled compressed air-cooled Photo-CDR base. (1) Photo-CDR, (2) recess for housing a temperature probe, (3) air-cooled base, (4) fluid port ¼ 28 UNF threads, (5) compressed air input, (6) air conduit.



Supplementary Figure 5: TechdrawCAD design file showing plan of lower part of the lamp holder for shrouding the compressed air-cooled Photo-CDR base.

Print parts from the stl files (material in parenthesis).

1 x Compressed air-cooled base (PLA)

1 x Lamp holder lower (PLA)

1 x Lamp holder upper (PLA)

1 x Vented cap (PLA)

(optional) 1 x Adapter for Hepatochem lamps (PLA)

1 x each of the lamp spacers (PLA)

1 x Photo-CDR (PP)

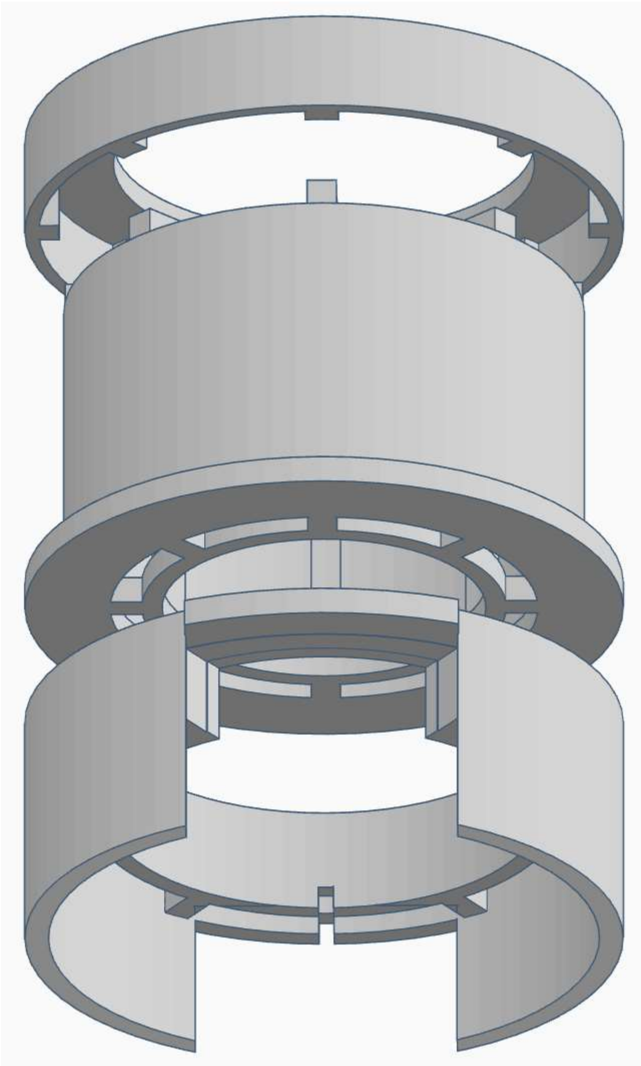
(optional) 1 x Photo-CDR with temperature probe housing (PP)

Remove the brim from all printed parts with a sharp craft knife or scalpel.

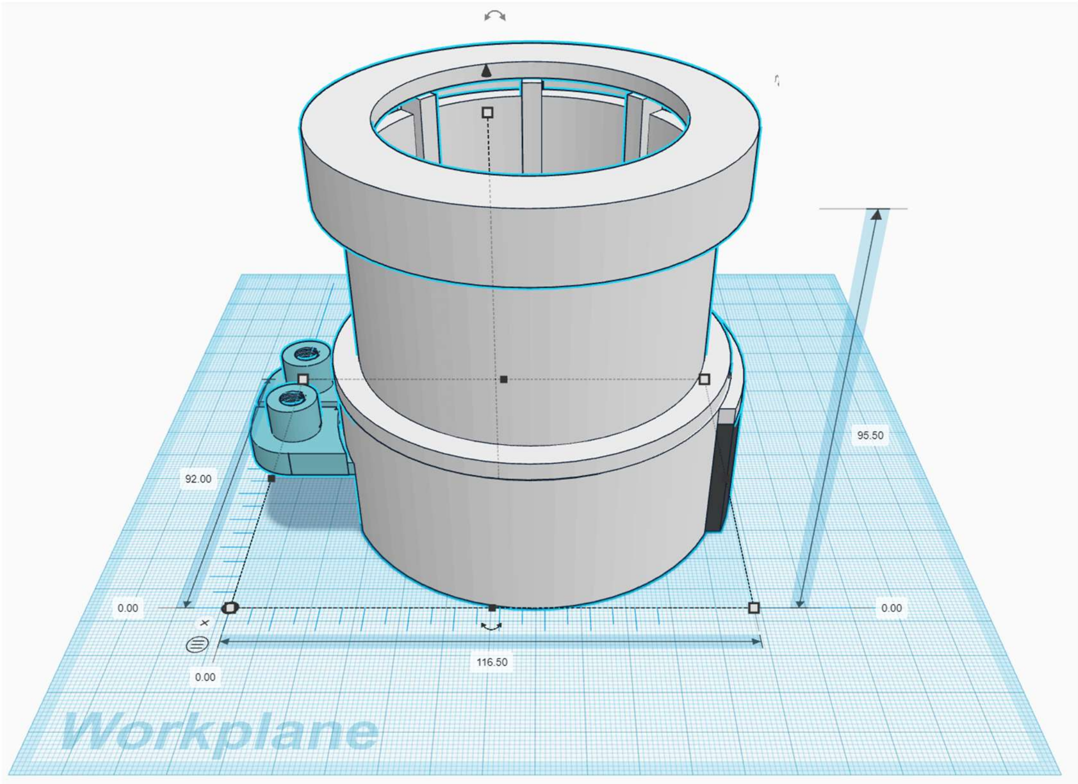
Commercially sourced parts

PK of 6 Mirror Circle / Acrylic Mirror Disc - 70 mm diameter

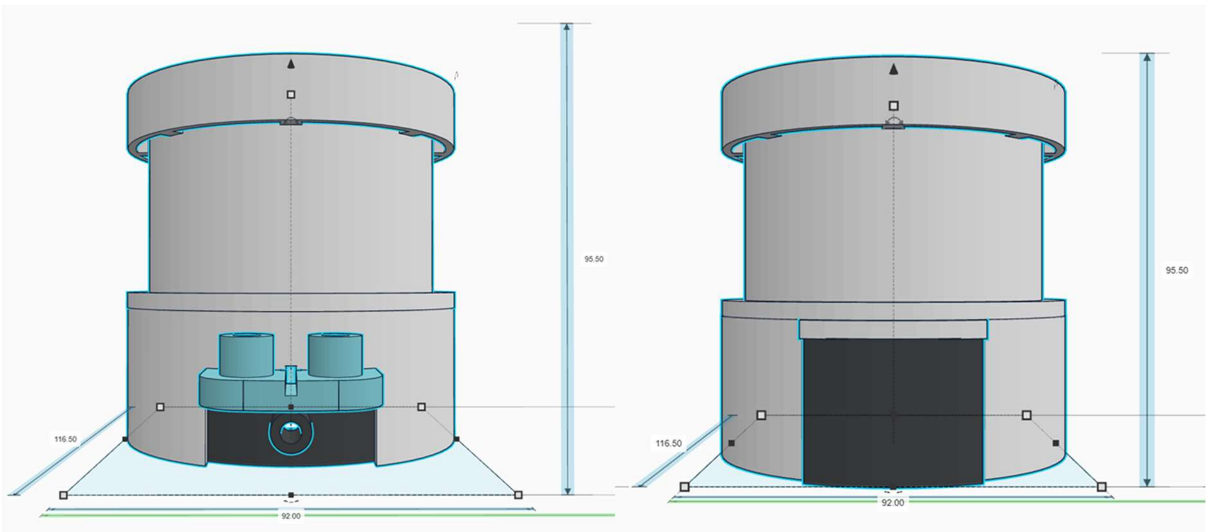
Supplier: eBay Item number 282569517759



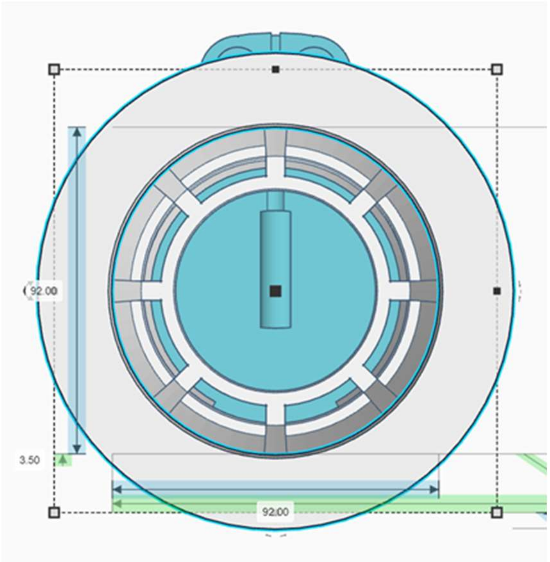
Supplementary Figure 6: TinkerCAD exploded view (underside) of the lamp holder base, lamp holder and vented cap.



Supplementary Figure 7: TinkerCAD file showing assembled air-cooled lamp holder.



Supplementary Figure 8: TinkerCAD file showing assembled air-cooled lamp holder front and rear elevation.



Supplementary Figure 9: TinkerCAD file showing assembled air-cooled lamp holder above view showing Photo-CDR (shown in cyan) with central recess for temperature probe

S2.3. Assembly of the 3D-printed components

S2.3.1. Compressed air-cooled Photo-CDR base

Remove the printing support from underside of the compressed air input by twisting the plastic support along horizontal and vertical break lines. Affix appropriate connector to the compressed air supply line.

Line the inner of the Photo-CDR base with reflective mirror tape or foil to act as a reflector and using a polypropylene glue gun (or epoxy glue) apply glue to the lower rim and fix in position the mirror at the bottom of the Photo-CDR base (figure 10).

Supplementary Figure 10: Assembled compressed air-cooled Photo-CDR base with mirror inserted and air input adapter attached.

S2.3.2. Assembly of the lamp holder

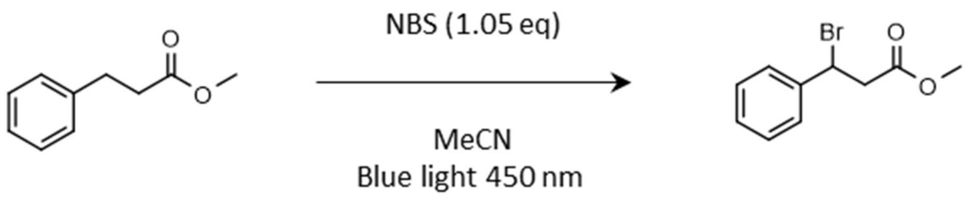
Line the inner face of the lower part of the lamp holder that will sit above the Photo-CDR with the reflective mirror tape or foil. Using the same glue gun or epoxy glue as previously, glue the top of the lower part of the bottom of the upper part of the lamp holder and leave to set secure (see exploded view figure 6, assembled views figures 7 & 8).

S3. General Flow Procedure

A pressure-driven IKA-Flow continuous flow system was setup with 450 nm blue LED lamps held at a fixed distance of 25 mm above a single Photo-CDR (Figure 1). Back-pressure was achieved in the flow system by either using a capillary resistor (length 100 mm, ID 0.18 mm), or using a 3D-printed back-pressure regulator (BPR) [3]. The BPR was operated with IKA-Flow system pressure set at 15 psi and the BPR set at 14 psi to control a flow rate of 0.5 mL min^{-1} using carrier solvent of acetonitrile (Figure 1). The lamp was turned on (intensity 100%) and compressed air cooling applied to stabilise the temperature of the Photo-CDR before introduction of reactants. A 0.5 M solution of substrate (1 eq) and *N*-bromosuccinimide (1.05

eq) in acetonitrile was prepared and sparged with a stream of nitrogen. 2 mL of the reactant solution was injected into the flow system at a flow rate of 0.5 mL min^{-1} using acetonitrile as the carrier solvent. See Figures 1 & 2 for full apparatus set up.

As in the previous publication, we selected the bromination of methyl hydrocinnamate to act as a standard reaction for comparison [1] (Scheme 1). As previously, conversion of starting material to product was determined by ^{1}H-NMR. Conversion (%) was determined by relative integrals of the methyl singlet of the methyl ester. Unlike the previous published methods, the pure brominated product was not isolated on this occasion.



Scheme 1. Selected radical bromination photochemistry reaction for photoCDR testing.

Table 1 - Results

Entry	light source (450 nm)	Power (W)	T (°C)	Conv.(%)
1	Kessil H150W	32	58	74
2	Hepatochem	18	65	24

S4. Raspberry Pi Thermocouple Datalogger

S4.1. Bill of materials

Description	Product Number	Source	Price (£)
Raspberry Pi 4 Model B 2Gb	SC0193	thepihut.com	33.90
Official UK Raspberry Pi 4 Power Supply (5.1V 3A)	SC0212	thepihut.com	7.50
Raspbian Preinstalled 16GB Micro SD Card [Discontinued]	SC0267	thepihut.com	8.00

Thermocouple Amplifier MAX31855 breakout board	ADA269	thepihut.com	13.00
Thermocouple Type-K Glass Braid Insulated Stainless Steel Tip	ADA3245	thepihut.com	8.70
RGB LCD Shield Kit w/ 16x2 Character Display	ADA716	thepihut.com	20.80
3D Printing Filament Made in Germany 1.75 mm 2.85 mm PLA PETG HIPS 15 Colours 1 kg Spool or Refill	8719689844059	amazon.co.uk	(24.88/ kg, 71 g used) 1.77
Total			(116.78) 93.67

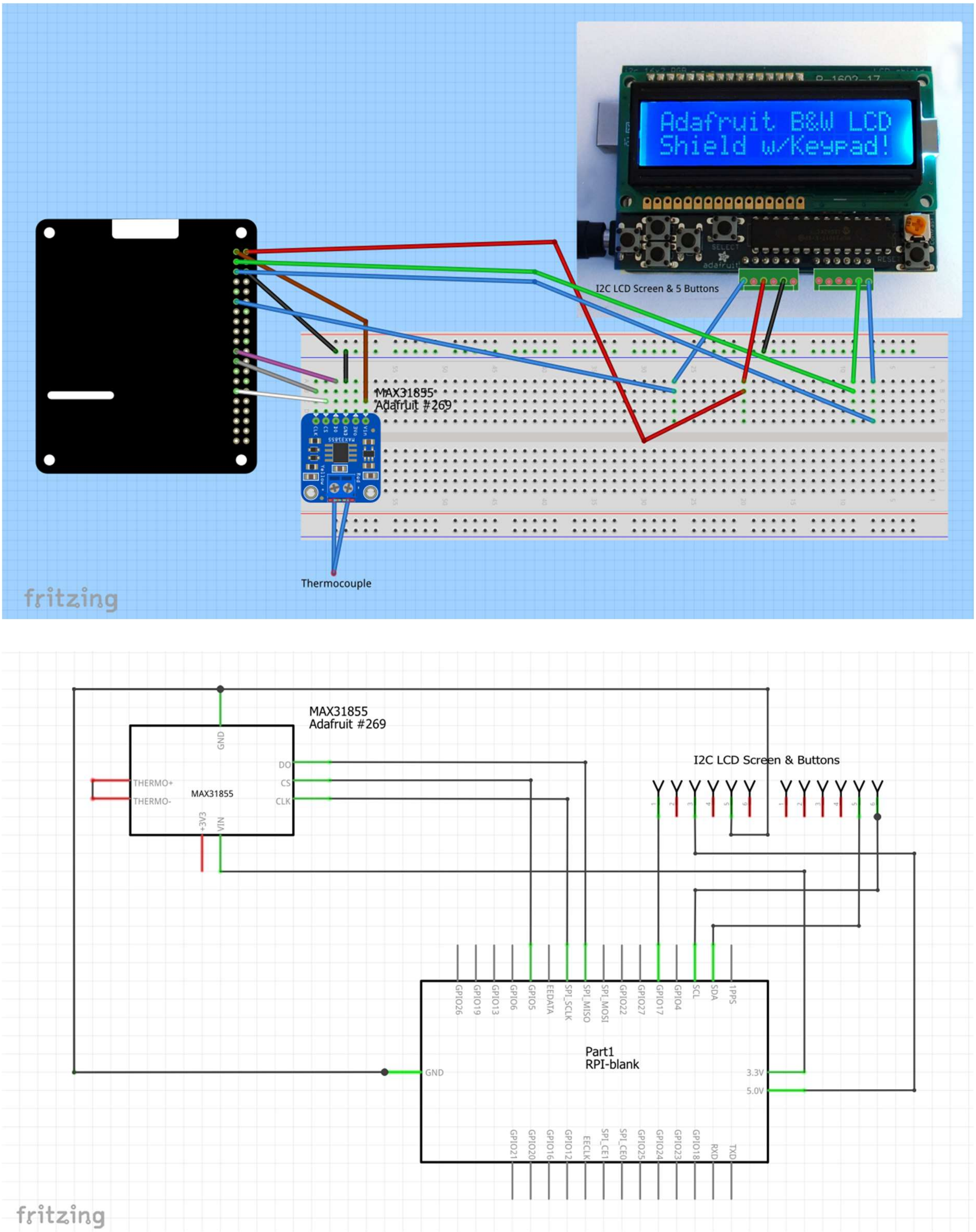
A modified version of a publicly available Raspberry Pi 4 case [4] was designed to accommodate RGB LCD shield (ADA716) – allowing headless operation of the device and containment of all components. STL files are available at https://github.com/vernalis/3Dprint_files. This was printed in PETG filament to provide good temperature resilience during operation even during high CPU usage.

S4.2. Assembly

Raspberry Pi 4 containing 16Gb SD card (with operating system pre-installed) was fitted into the base of the case. See Figure 11: Fritzing diagram below for clarification of GPIO circuitry.

Thermocouple amplifier (ADA269) interfaces using SPI and was connected to 3V (Vin), Ground (Gnd), GPIO 9 (Do/MISO), GPIO 11 (Clk) and GPIO 5 (CS). Type-K class thermocouple (ADA3245) was connected to positive and negative terminals, noting correct polarity [5]. Thermocouple threaded through side port included in upper portion of case.

RGB LCD Shield (ADA716) was constructed according to supplier instructions [6]. The screen and buttons primarily interface using I2C, with the reset button operating as an independent switch monitored on a separate GPIO pin. Shield was connected to 5V, Ground, GPIO 2 (Data/SDA), GPIO 3 (Clock/SCL) and GPIO 17 (Reset, configured pin to be ‘pull up’). Screen was then mounted into upper portion of case using 4 x M2.5 bolts (M2.5 nuts printed into the casing). Case could then be snapped together closed.



Supplementary Figure 11: Fritzing & electrical circuit diagrams

S4.3. Code

Datalogging code written and tested in Python 3.7.3 using Thonny IDE. Thermocouple interface code based on that supplied by manufacturer [5]. Screen I2C interface code based on that supplied by manufacturer [6].

Once started, the code will log a temperature every 15 seconds to a csv file in a pre-defined file location and update the LCD screen accordingly. To prevent log file corruption, press and hold the reset button to 'break' and stop the code loop.

Code is made available at https://github.com/vernalis/digital-lab

References

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   This content is a preprint and has not been peer-reviewed.

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