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Additive manufacturing of intricate and inherently photocatalytic flow reactor components

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Abstract

A 2,1,3-benzothiadiazole-based photosensitiser has been successfully incorporated into a commercially available 3D printing resin and utilised to fabricate inherently photocatalytic flow reactor components. The freedom of design provided by additive manufacturing enabled the production of photoactive monolith structures with intricate architectures, imparting functionality for heterogeneous photocatalysis and interesting manipulation of fluid dynamics within a fixed bed reactor column. The resultant monoliths were applied and validated in the photosensitisation of singlet oxygen in aqueous media, under continuous flow conditions and visible light irradiation (420 nm). The photo-generated singlet oxygen cleanly converted furoic acid to the γ -lactone, 5-hydroxy-5H-furan-2-one, with a peak space-time yield of 2.34 mmol m⁻² h⁻¹ achieved using the Voronoi monolith.

Keywords: 3D printing, flow technology, metal-free organic photosensitiser, singlet oxygen

1. Introduction

Within the last decade, additive manufacturing (AM) has emerged as an enabling technology for the fabrication of complex 3D components. With 3D printer technology becoming increasingly affordable and

1 accessible, it seems inevitable that this technology will continue to be ever more present as a standard
2 accessory of research institutions. AM has already found much utility within chemical science, especially
3 for biomaterials research where AM has enabled the fabrication of biocompatible scaffolds that permit cell
4 growth in three dimensions to imitate organs [1].

5 More recently, the focus of AM research has shifted to the fabrication of functional materials for
6 a variety of applications, including heterogeneous catalysis. The freedom of design offered by AM enables
7 the production of complex material architectures with high surface area and static mixing capabilities; ideal
8 support materials for heterogeneous catalysts [2]. Monolithic structures with various metal and metal oxide
9 catalysts have been fabricated *via* fused deposition modelling (FDM) for synthetic applications, such as a
10 cylindrical lattice printed from Al₂O₃ ink which acted as a heterogeneous Lewis acid catalyst in the
11 synthesis of dihydropyridines and dihydropyrimidinones [3]. Cronin and co-workers have also prepared
12 reactionware *via* FDM, which incorporated montmorillonite K10 Lewis acidic clay in one reaction chamber
13 and palladium on charcoal (Pd/C 10%) hydrogenation catalyst in a separate chamber, both of which were
14 printed from specially prepared 'ink' materials [4].

15 FDM has some limitations for the fabrication of flow reactor devices; the nature of printing layer-to-layer
16 creates anisotropy in the material, as well as voids between the individual layers. This affects the
17 mechanical properties of the printed material and, more importantly for flow reactors, can affect the '*water*
18 *tightness*' as solution can percolate through the voids and present leaks [1,5]. Stereolithography (SL) is
19 another form of AM which overcomes these obstacles. SL 3D printers' function through vat-
20 photopolymerization of a liquid resin. The individual layers are covalently crosslinked, providing materials
21 that are isotropic in all three dimensions, with no macroscopic grain structure or voids [1,5]. As SL 3D
22 printers use liquid resins to form materials, catalysts with polymerizable functional groups can be easily
23 incorporated into the resin, which results in the direct fabrication of functional materials.

(A) Previous Work: Photocatalytic Flow Reactor

- ❌ Photocatalyst in external surfaces block light from active sites in flow channels
- ❌ Simple 2D design; could be manufactured conventionally

(B) This Work: Photocatalytic Monoliths

- ✓ Intricate 3D designs
- ✓ Non-Commercially available, nor easily manufactured through conventional methods

- ✓ Active surfaces irradiated directly
- ✓ Improved gas-liquid reactivity
- ✓ Rapid prototyping

Figure 1: Comparison of disadvantages of A) previously reported SL manufacture of flow reactors and B) advantages of the manufactured functional monoliths presented in this work.

Recently we present the first example of this methodology for the production of inherently photocatalytic 3D printed flow reactors (Figure 1A) [6]. However, we identified several issues and failed to take full advantage of the freedom of design offered by AM. Herein, we address those issues and have utilised AM's freedom of design to fabricate intricate structures with potential for static mixing functionality. Four unique monolith structures have been fabricated and compared for efficiency, as well as analysing their effect on mixing performance through residence time distribution (RTD) studies (Figure 1B). The materials were then successfully applied as singlet oxygen ($^1\text{O}_2$) generators for the conversion of 2-furoic acid (**1**, Scheme 2) to the γ -lactone, 5-hydroxy-5H-furan-2-one (**2**, Scheme 2), in continuous flow.

2. Material and methods

2.1 Design and fabrication of monoliths

Following our previous '*proof of principle*' study on the SLA fabrication of a photoactive microfluidic device, we identified some obstacles that we wished to address in this report [6]. Primarily, the irradiation of the 3D printed surface in contact with the reaction solution was suboptimal in the microfluidic device, as the external surfaces of the reactor also contained photocatalyst which attenuated a significant amount of the incident irradiation, limiting the efficiency of the device. To overcome this, we have designed monolithic structures that are compatible with a fixed bed reactor, such that the surfaces in contact with the flowing reagents are directly exposed to the irradiation. We also wished to demonstrate and take full

advantage of the freedom of design offered by 3D printing. Hence, four cylindrical monolith designs were produced with increasingly intricate designs. **D1** has a simple two-dimensional channel structure, parallel and perpendicular to the long axis of the monolith. **D2** is identical to **D1**, except the perpendicular channels are removed, forming a typical honeycomb type monolith design. The **Voronoi** and **Gyroid** designs are more complex, generated from a *pseudo*-random lattice and periodic lattice, respectively (Figure 2). Details of the designs and their generation can be found in the ESI (Section S4).

Figure 2: Computer-aided design (CAD) diagrams of the 4 different monolith designs with key geometric parameters (L = length, W = width, V = internal volume, SA = surface area).

2.2 Optimisation of printing parameters for varied photocatalyst loadings

The commercial resin used was Formlabs Clear Resin (FLGPCL05, Formlabs Inc., Somerville, MA, USA), which is composed of a urethane dimethacrylate (55-75%), methacrylate monomer(s) (15-25 %) and photoinitiator (<0.9%) (Scheme 1). We chose to use 4,7-di(4-vinyl)phenylbenzo-2,1,3-thiadiazole (**St-BTZ**, Scheme 1) as a photocatalyst monomer, as the vinyl groups are compatible with the acrylates resin during the photopolymerization process (Scheme 1). Details of the **St-BTZ** monomer synthesis and characterisation can be found in the ESI (Section S2).

Scheme 1. Structure of **St-BTZ** and representative structures of methacrylate, urethane dimethacrylate and photoinitiator molecules which are the major components of the commercial resin. The exact structures are a trade secret and hence the identity of the photoinitiator, R-groups and chain lengths are unknown. A representative structure of the printed polymer material **P(St-BTZ)** is also given. Dashed bonds indicate a continuation of the polymer chain structure with any of the three monomer units, or a terminal capped with photoinitiator, in proportions respective of the resin composition.

3D printed prototypes were produced using a digital light processing (DLP) printer (PICO 2HD 27UV, Asiga). The LED system of the DLP printer irradiates at 385 nm, which the **St-BTZ** monomer also absorbs (*vide infra*). This seems intuitively problematic; however, this can reduce over-irradiation and improve printing resolution. To account for this, we first assessed the effect of the photocatalyst additive on the polymerisation kinetics *via* double bond conversion (DBC) rates. Real-time FTIR spectroscopy was used to monitor the C=C stretching frequency of the vinyl and acrylate monomers at around 1620-1650 cm⁻¹ as a function of time, while the sample was irradiated at 365 nm. The change in absorption intensity can be used to calculate DBC following Equation 1.

$$DBC = \left[\frac{A_0 - A_t}{A_t} \right] \times 100 \quad (1)$$

Where the DBC is proportional to the initial absorption intensity before irradiation (A_0) and the absorption intensity after a given irradiation time (A_t). An example of the depleting signal intensity over time during irradiation is given in Figure 3A for the native resin with no **St-BTZ** additive. The effect of increasing **St-BTZ** concentration on the polymerisation kinetics is shown in Figure 3B. Individual absorption traces for each of the concentrations can be found in the ESI (Section S3).

Figure 3: A) Real-time FTIR spectra of Formlabs Clear resin with 0 wt.% **St-BTZ**. B) DBC (%) vs. time trace for various **St-BTZ** wt.% loadings.

Addition of **St-BTZ** caused an increase in both the rate of polymerisation and the overall DBC value obtained. The trend between rate, DBC and **St-BTZ** wt.% was relatively linear, except for 0.19 wt.% **St-BTZ** which had the fastest kinetics and highest overall DBC. We attribute this to be due to a balance between light attenuation and photosensitised acceleration of the photo-polymerisation (See ESI, Section S3) [7,8].

3. Results

3.1 Photophysical characterization

St-BTZ displays a broad absorption profile in the range of 350–450 nm, with a maximum absorption intensity (λ_{max}) at approximately 380 nm (**Figure 4A**) [9]. This is almost perfectly aligned with the 385 nm light source of the DLP printer used for device fabrication. Adding **St-BTZ** to the resin resulted in an increase in absorption around the 350–450 nm region (**Figure 4A**). The peaks of the native resins are still visible up to 0.19 wt.%. At 1 wt.%, the light attenuation of the sample becomes too great and the definition of the profile is lost. Thin films of the 3D printed material were fabricated and analysed by solid-state UV-Vis. spectroscopy for comparison. The solid samples showed an increasing absorption intensity around the 350-500 nm region with increasing **St-BTZ** concentration, as shown in **Figure 4B**.

Figure 4: UV-vis absorption spectra of (A) Formlabs Clear resin with different **St-BTZ** concentrations (diluted in IPA) and (B) Solid-state UV-Vis. absorption spectra of 3D printed films with various **St-BTZ** concentration. The solution-state absorption spectrum of the St-BTZ monomer (CHCl_3) is shown as a dashed, light-blue line in both graphs for reference, with the Y-axis shown on the right.

The λ_{max} undergoes a bathochromic shift with increasing **St-BTZ** concentration, comparable to the maximum absorption wavelength (420 nm) reported by Tobin *et al.* for poly(styrene-co-DVB-co-(St-BTZ)) [9]. The spectral profile of the 1 wt.% **St-BTZ** film deviates from the other samples, showing a far greater bathochromic shift in absorption maximum to 440 nm and the emergence of an absorption from 500-600 nm. We found that higher **St-BTZ** content exceeded the solubility limit, leading to aggregation of the photocatalyst monomer. These macroscopic aggregates were visible in the printed films and altered the absorption profile through light scattering. Following these results, 0.19 wt.% of **St-BTZ** was concluded as the optimal loading for providing the highest concentration of photosensitiser whilst maintaining a homogeneous resin mixture.

3.2 Monolith fabrication and RTD analysis

We proceeded to optimise the curing parameters for the photocatalyst-doped resin within the DLP printer, the results of which are tabulated in the ESI (Table S3). To confirm our results from the RT-FTIR kinetic analysis described in section 2.2, we printed prototype structures with each of the resins and found that the higher wt.% loadings required significantly higher exposure times (c.f. 0 wt.% optimised exposure time = 0.68 seconds, vs. 1 wt.% optimised exposure time = 9 seconds). After printing and washing in isopropanol, the monoliths were post-cured for one hour via Asiga Flash UV post-curing chamber (type DR-301C, 36 W, 365 nm, Asiga). This shows that despite the enhanced kinetics of the polymerisation in the presence of photocatalyst, the subsequent light attenuation of the photocatalyst at greater curing depths did require a greater energy dose for successful printing, consistent with our previous report using an SLA printer [6].

We then fabricated the designs described in the first section using our established optimal loading of 0.19 wt.% **St-BTZ**. Images of the cured monolith structures can be seen in Figure 5A. The printed monoliths

pleasingly displayed the yellow colour of the **St-BTZ** monomer and showed no obvious defects or inhomogeneity. The fluorescence of the material was observed qualitatively by irradiating with a UV lamp, which also showed a uniform emission throughout the fabricated monoliths (Figure 5B). The finer details of the prints were observed under a microscope with a calibrated scale (Figure 5C & 5D), revealing the channel void spaces of the **D2** and **Voronoi** monoliths were within 20% error of the intended designs following the post-curing process (c.f. 874 μm vs. 750 μm).

Figure 5: (A) 3D printed and cured photo-active monoliths with 0.19 wt% **St-BTZ** concentration. (B) Image of the monoliths under long-wave UV irradiation, showing the blue glow of the incorporated **St-BTZ** monomers (from top to bottom: **D1**, **Gyroid**, **Voronoi**, **D2**). (C) Microscope image of the **Voronoi** monolith with length (L) of a diamond shaped void given for reference. (D) Microscope image of a cross section of the **D2** monolith with channel diameter (D) given for reference.

The qualitative analysis of RTD can be used to detect deviation from ideal plug flow and mixed flow behaviours, which can be caused by stagnant regions, channelling, and recycling of fluid. We proceeded to test the monolithic structures effect on the RTD for a single-phase solution flow stream and biphasic solution-gas flow stream at varying flow rates. This study was performed using an optical tracer (methyl orange) in the solution phase and monitoring the absorption intensity of the outflow stream. A detailed discussion of the RTD experimental procedure and parameter derivations can be found in the ESI (Section S6), and the RTD profiles obtained are displayed in Figure 6 & 7. RTD is frequently described by the mean

1 residence time (τ), variance (σ^2) and reduced variance (σ_θ^2), which were obtained and are displayed in the
2 ESI (Tables S4 for solution and Table S5 for solution-gas flow regimes).

Figure 6: Comparison of residence time distribution of the monolith designs – a) RTD and b) normalized RTD curves at the liquid flowrate of 0.1 mL min^{-1} ; c) RTD and d) normalized RTD curves at the liquid flowrate of 0.5 mL min^{-1} ; e) RTD and f) normalized RTD curves at the liquid flowrate of 1 mL min^{-1} .

In case of the single-phase liquid flow, the pulse response is broad and non-symmetrical, with the presence of tailing. This represents a flow pattern between plug flow and laminar flow at all flowrates (0.1, 0.5 and 1 mL min^{-1}), as shown in Figure 6. As expected, the D2 design provided the shortest mean residence time

compared to other monolith designs ($\tau = 20.6$ min at 0.1 mL min^{-1} ; $\tau = 4.9$ min at 0.5 mL min^{-1} and $\tau = 2.6$ min at 1 mL min^{-1}), concurrent with **D2** possessing the lowest internal volume of all the monolith structures. The normalised RTD ($E(\theta)$) curves (Figure 6B, 6D & 6F), which are independent of reactor size, were nearly identical at the flow rate of 0.5 mL min^{-1} for all 4 monolith designs. The $E(\theta)$ curves show an early peak and the presence of tailing, indicating back mixing due to a parabolic flow profile, which is associated with laminar flow [10,11]. When the flowrate was increased to 1 mL min^{-1} , the **D2** and **Voronoi** designs showed slight deviations as the peak shifted to the left of the mean residence time ($\theta = 1$), and exhibiting an increase in the spread of the curve, highlighted by an increase in σ_{θ}^2 (ESI, Table S4). At the flow rate of 0.1 mL min^{-1} , **D2** significantly shifts away from $\theta = 1$, indicating a significant increase in stagnant regions [11,12].

Performing the same analysis with a biphasic flow of gas and liquid provided similar results; all monolith designs provided near identical normalised RTD profiles (Figure 7). Compared to single-phase flow, the maximum $E(\theta)$ values were shifted to slightly lower θ values in the biphasic flow system and the form of the RTD profiles had changed. This indicates presence of bypassing and dead zones, which reduces the effective reactor volume, so the active reactor volume (available for liquid phase flow) is smaller than expected [13].

Figure 7: Comparison of residence time distribution of the monolith designs – a) RTD and b) normalized RTD curves at the liquid flowrate of 0.5 mL min⁻¹ and gas flowrate of 1.6 mL min⁻¹; c) RTD and d) normalized RTD curves at the liquid flowrate of 1 mL min⁻¹ and gas flowrate of 2.3 mL min⁻¹.

3.3 Singlet oxygen photosensitisation efficiency

We proceeded to test the efficiency of the fabricated monoliths for singlet oxygen (¹O₂) photosensitisation, using the oxidation of aqueous 2-furoic acid (**1**, Scheme 2) as a model reaction to gauge efficiency. The mechanism of generating photosensitised singlet oxygen is well studied and proceeds as illustrated in Scheme 2 [2,14,15]. More detailed discussion of the mechanism can be found in the ESI (Section S8). Unlike other reactive oxygen species, ¹O₂ is a singlet diradical which imparts much greater chemoselectivity for (2n)π systems, such as alkenes, dienes and heteroatoms. For 5-membered aromatic heterocycle substrates, such as **1**, singlet oxygen reacts exclusively *via* an Alder-ene [4+2] cycloaddition to give the endoperoxide **I** [16]. This unstable intermediate readily decarboxylates and ring-opens the endoperoxide. The subsequent protonation yields the γ-lactone product, 5-hydroxy-5H-furan-2-one **2** [2,17].

Scheme 2: Mechanism of singlet oxygen photosensitisation by **P(St-BTZ)** and subsequent oxidation of 2-furoic acid **1** to γ-lactone, 5-hydroxy-5H-furan-2-one **2**. +hv = photon absorption, -hv_f = fluorescence photon emission, ISC = intersystem crossing, TTA = triplet-triplet annihilation.

The lifetime of ¹O₂ is highly dependent on solvent and temperature due to electronic-to-vibrational energy transfer facilitating non-radiative decay back to the ³O₂ ground state [18,19]. Counterintuitively, we elected to use water as the solvent in our system which provides the lowest singlet oxygen lifetime of all common laboratory solvents (3.1 μs) [20]. This was for a few reasons: (i) water is considered a green solvent, (ii) substrate **1**, product **2** and ³O₂ have good solubility in water, (iii) the monolith polymer materials are

relatively hydrophobic, such that water will not cause the monoliths to swell and distort the structures, (iv) photosensitised singlet oxygen is a promising candidate for environmental remediation of waste water [21–23].

We screened the performance of the four monolith designs at three flowrates with a total cycling time of 3 hours. The results are presented in the ESI (Table S6), and a comparison of total conversion over 3 hours and space-time yields vs. flow rate for each design is presented in Figure 8.

Figure 8: Influence of the flowrate on the 2-furoic acid conversion in 3D printed monoliths and the space-time yield (STY). Reactions were cycled in a continuous loop through the reactor for a total of 3 hours. The net flow rate is the combined flow rate of the gas and solution phases from their respective pump. In all cases, the flow rate of gas and solution were equivalent.

All designs were capable of photosensitising singlet oxygen and subsequently producing **2**. As was anticipated, the **D2** monolith provided the lowest conversion and STY across all three flowrates, except for 1 mL/min at which **D2** surpassed the **Gyroid** designs conversion by 1%, which is within the error of the ¹H NMR analysis. **D1** and **Voronoi** proved to be the optimal designs as they maintained the highest conversion across all flow rates. As the experiments were performed with continuous recycling of the same reaction mixture, the total residence time and light exposure is constant for all flow rates and designs (180 minutes). Hence, we can assume that the difference in productivity between designs is entirely dependent upon the surface area, fluid dynamics and the efficiency of photon transport through the structures. **D1**, **Voronoi** and **Gyroid** achieved the highest conversions and STYs at the lowest net-flow rate tested. This was counter-intuitive as usually static mixing elements will display better mass transport and increased gas-liquid

interfacial area at higher flow rates [24]. We propose as the total irradiance time for each flow rate is constant, the lower flow rate is providing the best fluid dynamics and distribution of the gas and liquid phases, leading to the enhanced productivity.

D2 followed the trend expected for a static mixing element, however the magnitude of the enhancement between 0.2 and 1 mL/min was surprising. In fact, at the fastest net-flow rate of 2 mL/min, **D2** had a higher space-time yield than the more intricate designs at either 1 or 2 mL/min. Rationalising this was not immediately obvious, however, Billet and co-workers reported that traditional ‘honeycomb’ monoliths display maldistributed gas-liquid phase distribution, depending on flowrate [25]. At low flow rates, the distribution of the liquid phase is concentrated to the center channels, and at higher flowrates the distribution is more uniform. We believe that this same effect is occurring within the **D2** monolith design as this forms a logical rationale for our experimental observations: The channels of the **D2** design were contained within a cylinder such that photons had to pass through a solid layer of **P(St-BTZ)** material to activate the channel surfaces. As can be seen in Figure 5, the wall thickness between the outer channels and the monolith exterior are relatively thin and transparent, whereas the internal channels are completely masked by the outer layers, and likely receive very little irradiance. The RTD analysis of the **D2** monolith for the monophasic liquid flow at 0.1 mL min⁻¹ was suggestive of this effect, unfortunately the biphasic RTD profile could not be obtained at such low flow rates due to the long residence time of gas slugs in the spectrometer. We instead fabricated the **D2** monolith using the native clear resin and repeated the RTD analysis without the spectrometer, in an attempt to visualize the maldistribution as the tracer passed through the immobilized monolith. Gratifyingly, this effect was easily observed and captured with a camera (see ESI, Figure S3). The tracer could be clearly seen passing through a single channel of the monolith as primarily a single phase, whilst other channels remained relatively stagnant. This confirmed our speculation of maldistribution and supports our rationalization of the photosensitization efficiency of the **D2** monolith at varied flow rates.

In all cases, the efficiency of these reactors was significantly greater than the flow reactor published in our previous study, which obtained 5% conversion of **1** to **2** in 5 hours, under near identical conditions [6].

4. Conclusions

This study has demonstrated stereolithographic additive manufacturing as a methodology for the rapid prototyping of flow reactor components. Functional materials were produced *in situ* through addition of a photocatalytic monomer to a commercial resin, enabling fabrication of heterogeneous photocatalysts. Despite the St-BTZ monomer having significant spectral overlap with the DLP printers' light emission, stable monolithic structures with photocatalytic ability were successfully fabricated through printing parameter optimisation. Successful incorporation of St-BTZ was confirmed by solid-state UV-Vis. spectroscopy and allowed the determination of 0.19 wt.% as an optimal loading to balance solubility, light attenuation and accelerated polymerisation kinetics within the resin. All fabricated monolith designs were capable of producing photosensitised singlet oxygen in continuous flow which was proven through the conversion of 2-furoic acid **1** to the γ -lactone, 5-hydroxy-5H-furan-2-one **2**. The effects of monolith structure and flow rate were investigated with surprising results, finding that the simplest design, **D2**, provided the highest space-time at high flowrates. We propose that maldistribution of the flowing gas and liquid phases was the productivity limiting factor in these designs, rather than mass transfer at the monolith surface. This study demonstrates AMs ability to rapidly fabricate reactor prototypes that are neither commercially available, nor easily produced through conventional manufacturing methods. This is a promising technology for the development of bespoke, multi-functional, flow reactor components for continuous production of fine chemicals through heterogeneous photocatalysis, with enhanced sustainability as the product purification requirements are reduced and the catalyst is easily recycled [2,26,27]. Furthermore, the development of easily manufactured and efficient heterogeneous photosensitisers for the generation of singlet oxygen in aqueous media is an auspicious move towards tackling significant issues within wastewater remediation. This includes the degradation of aqueous dyes and active pharmaceutical ingredients from industrial and urban wastewater sources, and the destruction of water borne pathogens to provide safe drinking water, using a mild and visible light (solar)-powered methodology [2,23,28–30].

5. Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. Acknowledgements

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(A) Previous Work: Photocatalytic Flow Reactor

- ❌ Photocatalyst in external surfaces block light from active sites in flow channels
- ❌ Simple 2D design; could be manufactured conventionally

(B) This Work: Photocatalytic Monoliths

- ✓ Intricate 3D designs
- ✓ Non-Commercially available, nor easily manufactured through conventional methods

- ✓ Active surfaces irradiated directly
- ✓ Improved gas-liquid reactivity
- ✓ Rapid prototyping

Figure 1: Comparison of disadvantages of previously reported SLA manufacture of flow reactors and advantages of the SLA manufactured functional monoliths presented in this work.

Scheme 1. Structure of **St-BTZ** and representative structures of methacrylate, urethane dimethacrylate and photoinitiator molecules which are the major components of the commercial resin. The exact structures are a trade secret and hence the identity of the photoinitiator, R-groups and chain lengths are unknown. A representative structure of the printed polymer material **P(St-BTZ)** is also given. Dashed bonds indicate a continuation of the polymer chain structure with any of the three monomer units, or a terminal capped with photoinitiator, in proportions respective of the resin composition.

Figure 3: A) Real-time FTIR spectra of Formlabs Clear resin with 0 wt.% St-BTZ. B) DBC (%) vs. time trace for various St-BTZ wt.% loadings.

Figure 4: UV/vis absorption spectra of (A) Formlabs Clear resin with different St-BTZ concentrations (IPA) and (B) Solid-state UV-Vis. absorption spectra of 3D printed films with various St-BTZ concentration. The solution-state absorption spectrum of the St-BTZ monomer (CHCl₃) is shown as a dashed, light-blue line in both graphs for reference, with the Y-axis shown on the right.

Figure 5: (A) 3D printed and cured photo-active monoliths with 0.19 wt% St-BTZ concentration. (B) Image of the monoliths under long-wave UV irradiation, showing the blue glow of the incorporated St-BTZ monomers (from top to bottom: D1, Gyroid, Voronoi, D2). (C) Microscope image of the Voronoi monolith with length (L) of a diamond shaped void given for reference. (D) Microscope image of a cross section of the D2 monolith with channel diameter (D) given for reference.

Figure 6: Comparison of residence time distribution of the monolith designs – a) RTD and b) normalized RTD curves at the liquid flowrate of 0.5 mL min⁻¹; c) RTD and d) normalized RTD curves at the liquid flowrate of 1 mL min⁻¹.

Figure 7: Comparison of residence time distribution of the monolith designs – a) RTD and b) normalized RTD curves at the liquid flowrate of 0.5 mL min⁻¹ and gas flowrate of 1.6 mL min⁻¹; c) RTD and d) normalized RTD curves at the liquid flowrate of 1 mL min⁻¹ and gas flowrate of 2.3 mL min⁻¹.

Scheme 2: Mechanism of singlet oxygen photosensitisation by **P(St-BTZ)** and subsequent oxidation of 2-furoic acid **1** to γ -lactone, 5-hydroxy-5H-furan-2-one **2**. $+h\nu$ = photon absorption, $-h\nu_f$ = fluorescence photon emission, ISC = intersystem crossing, TTA = triplet-triplet annihilation.

Figure 4: Influence of the flowrate on the 2-furoic acid conversion in 3D printed monoliths and the space-time yield (STY). Reactions were cycled in a continuous loop through the reactor for a total of 3 hours.

The following document details the individual author contributions in the CRediT system, to the manuscript:

Additive manufacturing of intricate and inherently photocatalytic flow reactor components

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