



Heriot-Watt University  
Research Gateway

# Additive manufacturing of photoactive polymers for visible light harvesting

## Citation for published version:

Zhakeyev, A, Tobin, J, Wang, H, Vilela, F & Xuan, J 2019, 'Additive manufacturing of photoactive polymers for visible light harvesting', *Energy Procedia*, vol. 158, pp. 5608-5614.  
<https://doi.org/10.1016/j.egypro.2019.01.579>

## Digital Object Identifier (DOI):

[10.1016/j.egypro.2019.01.579](https://doi.org/10.1016/j.egypro.2019.01.579)

## Link:

[Link to publication record in Heriot-Watt Research Portal](#)

## Document Version:

Publisher's PDF, also known as Version of record

## Published In:

Energy Procedia

## General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

## Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [open.access@hw.ac.uk](mailto:open.access@hw.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



10<sup>th</sup> International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

# Additive manufacturing of photoactive polymers for visible light harvesting

Adilet Zhakeyev<sup>a,c</sup>, John Tobin<sup>a</sup>, Huizhi Wang<sup>b</sup>, Filipe Vilela<sup>a\*</sup>, Jin Xuan<sup>a,c\*</sup>

<sup>a</sup>*School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK*

<sup>b</sup>*Department of Mechanical Engineering, Imperial College London, Exhibition Road, South Kensington Campus, London, SW7 2AZ, UK*

<sup>c</sup>*Department of Chemical Engineering, Loughborough University, Loughborough, UK*

## Abstract

In recent years, 3D printing has gained a great deal of attention in the energy field, with numerous reports demonstrating its application in fabrication of electrochemical devices. The near-complete freedom of design offered by 3D printing technologies make them very appealing, since complex 3D parts can be directly fabricated. However, its application in photochemistry and solar energy harvesting remains, so far, an uncharted territory. In this work, a photoactive monomer was incorporated into commercially available 3D printing resin, which was subsequently used to successfully fabricate 3D photosensitizing structures for singlet oxygen generation. Results indicate that the SLA fabricated small-scale (0.1 ml) photoactive continuous flow reactor shows activity in singlet oxygen synthesis reaction under visible light irradiation (420 nm).

© 2019 The Authors. Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

*Keywords:* 3D printing; photoreactor; solar energy harvesting; organic photosensitizer

## 1. Introduction

Solar energy is by far the largest resource, amongst renewable energy sources, providing our planet with more energy in 1 hour than all of the energy consumed by humans in an entire year.[1] The use of solar light in chemical synthesis has been a long-standing aim in photochemistry.[2] In recent years, it was demonstrated that conjugated porous polymers (CMPs) are well suited for light (solar energy) harvesting applications, such as photogeneration of

\* Corresponding authors. Tel.: +44-0-131-451-3293; fax: +44-0-131-451-3293.

*E-mail address:* J.Xuan@hw.ac.uk; f.vilela@hw.ac.uk

singlet oxygen ( $^1\text{O}_2$ ).[3] By incorporating a photoactive material into a polymer backbone, self-quenching effect can be potentially mitigated due to reduction of the concentration of photoactive material (when compared to the CMPs).[4]

The issues associated with batch photochemistry can be overcome by the use of continuous-flow microreactors in photochemical synthesis applications.[5] Continuous-flow microreactors are generally fabricated using traditional manufacturing techniques, such as soft lithography, injection molding, etching (glass and silicon) or hot embossing. These microfabrication techniques are time and labor consuming, requiring multiple processing steps, and are limited by the range of features that can be produced. Additive manufacturing (AM), also known as 3D printing, presented itself as a viable alternative for microfluidic device fabrication, in recent years.[6-8] Out of consumer oriented AM technologies, stereolithography (SLA) proved to be most promising in microfluidic applications due to its ability to directly produce complex three-dimensional (3D) parts, with near-complete design freedom.

The range of commercially available SLA materials is limited to a small number of polymers. It was reported that the use of light absorbers, tailored to the light source of a SLA printer, can result in improvements in resolution of the prints and allow flow channel miniaturization, without the need for any changes in hardware, making it useful for microfluidic device fabrication.[9] By introducing bespoke CMPs into SLA resin formulation, it is envisioned that when tailored to the light source of a SLA 3D printer, not only CMPs can be used as absorbers to improve resolution, but can add a photocatalytic functionality to the 3D printed structures and devices. In this work, we present the development of bespoke photoactive resins that would enable the application of SLA in direct manufacturing of continuous flow reactors, made of photoactive polymers. It was demonstrated how a photoactive monomer can be incorporated with commercially available stereolithography resin to directly 3D print functional continuous flow reactors for  $^1\text{O}_2$  generation under visible light irradiation.

## 2. Materials and methods

### 2.1. Preparation of photoactive resin

A photoactive monomer - 4,7-distyrene-2,1,3-benzothiadiazole (St-BTZ), was synthesized following the process described in detail in a previous study.[4] The photoactive St-BTZ unit was then incorporated into a commercial SLA resin (Clear FLGPCL02, Formlabs Inc.), composed of mixture of methyl methacrylate (MMA) based oligomers, monomers and a photoinitiator. St-BTZ (166 mg) was firstly dissolved in 30 ml of chloroform ( $\text{CH}_3\text{Cl}$ ) in an ultrasonic bath for 5 minutes. The solution was then added to a mixture of Clear Formlabs resin (33.15 g) and  $\text{CH}_3\text{Cl}$  (30 ml) and ultrasonicated for 2 hours. After ultrasonication, resulting mixture was then stirred under heating at 95 °C for 18 hours to remove  $\text{CH}_3\text{Cl}$  solvent and subsequently obtain St-BTZ (0.5 wt%)/MMA resin mixture.

### 2.2. Additive manufacturing of photoactive polymer

A SLA 3D printer (Form 1+, Formlabs Inc.) was used to test the prepared 0.5 wt% St-BTZ resin and fabricate specimens. It is equipped with a 405nm violet laser used to initiate the free radical polymerization of photo-resin. A layer thickness of 25  $\mu\text{m}$  was used in fabrication of prototypes throughout. To obtain the optical properties (known as “working curve”) of the prepared 0.5 wt% St-BTZ resin, the operation of the Form 1+ 3D printer was modified, where the tilting motion of the resin tank and build platform were removed. A CAD file of a film with 25 panels ranging from 50 to 1250 microns in thickness, and therefore with each panel receiving different energy exposure values, was used to obtain the working curve. Once the film was printed, the unpolymerized resin is cleaned off and the thickness of each panel was measured with a micrometer. All the 3D printed parts were designed in Creo Parametric 3.0 (PTC) CAD software.

### 2.3. General procedure for photocatalytic reaction under batch conditions

For the batch singlet oxygen photogeneration experiments, 3D printed 0.5 wt% St-BTZ polymer sample was pulverized into fine powder before dispersal in a solvent. To investigate the feasibility of the use of 3D printed 0.5 wt% St-BTZ polymer in singlet oxygen ( $^1\text{O}_2$ ) generation in water, oxygen was bubbled into aqueous St-BTZ(0.5 wt%)/PMMA dispersion ( $1 \text{ mg mL}^{-1}$ ) containing 1.5 mmol of 2-furoic acid, at the rate of  $15 \text{ mL min}^{-1}$ , while irradiated with blue light at 420 nm, with a LED module emitting with 28 W light output and a light intensity of  $3.5 \text{ W cm}^{-2}$  (OSA Opto Lights, OLM-018 series, Berlin, Germany) at a distance of 7 cm. The reaction solution was mixed for the whole duration of the reaction with a magnetic stirring bar. The conversion of the reaction was evaluated by recording  $^1\text{H}$  NMR spectra of aliquots removed from the reaction mixture at different time points, prior to which 0.5 wt% St-BTZ polymer was filtered off through a syringe filter.

### 2.4. General procedure for photocatalytic reaction in flow employing 3D printed prototype

A solution containing water (5 ml) and 2-furoic acid (11.2 mg, 0.1 mmol) was pumped through a 3D printed 0.5 wt% St-BTZ prototype reactor (0.1 ml total volume) at a flowrate  $0.1 \text{ mL min}^{-1}$ , using a peristaltic pump from a commercial flow reactor (easy-Photochem, Vapourtec Ltd.). Concurrently, oxygen was pumped through a second pump at the same flow rate ( $0.1 \text{ mL min}^{-1}$ ), mixing with the solution at a T-junction before entering the 3D printed reactor. The operating pressure was kept at 1.3 bar to ensure a steady stream of both the solution and oxygen. The 3D printed reactor was illuminated with a LED module emitting at 420 nm with 28 W light output and a light intensity of  $3.5 \text{ W cm}^{-2}$  (OSA Opto Lights, OLM-018 series, Berlin, Germany) at a distance of 7 cm, whilst the reaction solution was cycled for 5 hours. The conversion of the reaction was evaluated by recording  $^1\text{H}$  NMR spectra.

### 2.5. Characterization methods

$^1\text{H}$  NMR spectra were recorded on a Bruker AVIII 300 spectrometer at 300.1 MHz at ambient temperature in deuterium oxide ( $\text{D}_2\text{O}$ ). UV/Vis absorption spectra were measured on Perkin Elmer Lambda 950 spectrometer. 3D printed object was observed with Focused Ion Beam (FIB) Emission Scanning Electron Microscopy (SEM, FEI Quanta 3D FEG).

## 3. Results and discussion

### 3.1. Additive manufacturing of photoactive polymer

The concentration of St-BTZ was chosen to be 0.5 wt% in this study, since it is limited by its solubility in a commercial MMA based resin. The working curve model was used to obtain resin optical properties. This model describes the thickness of the polymer that forms as a result of light absorption. As light passes through an absorbing media its intensity decays in an exponential fashion. When a photopolymer resin absorbs enough energy (critical energy), it undergoes a very rapid transition from a free flowing liquid to a gel like state. After critical energy is reached, the cured layer then slowly grows in thickness away from the light source. This model can be expressed by a modified Beer-Lambert law in terms of energy, and then solving for the thickness of the cured layer:

$$C_d = D_p \times \ln\left(\frac{E}{E_c}\right) \quad (1)$$

where,  $C_d$  is the resulting curing depth and  $E$  is the exposure energy. The penetration depth ( $D_p$ ) describes the penetration of light into the resin for all of the resin components, and critical energy ( $E_c$ ) describes how much energy the resin requires to cure, both of these constants determine the optical properties of a given resin. The working curves for Formlabs Clear resin with and without 0.5 wt% St-BTZ, are shown in Fig. 1a. It can be observed that the addition of 0.5 wt% St-BTZ significantly affects the resin optical properties. The penetration depth is decreased from  $318 \mu\text{m}$  to  $57 \mu\text{m}$ , while critical energy exposure is increased from  $37.5 \text{ mJ cm}^{-2}$  to  $693 \text{ mJ cm}^{-2}$ , when 0.5 wt% St-BTZ is

added into the resin. This can be explained by the fact that UV–Vis absorption spectrum for St-BTZ appears as a broad absorption peak in the range 350–450 nm with a maximum absorbance at 400 nm.[4] When incorporated into the commercial Formlabs Clear resin, it significantly increased the absorption of the resin at 405 nm, as shown in Fig. 1b. Since the Form 1+ 3D printer is equipped with a 405 nm laser, a significant portion of the energy supplied is subsequently absorbed by St-BTZ monomers in the resin, thus increasing critical energy exposure and decreasing penetration depth.

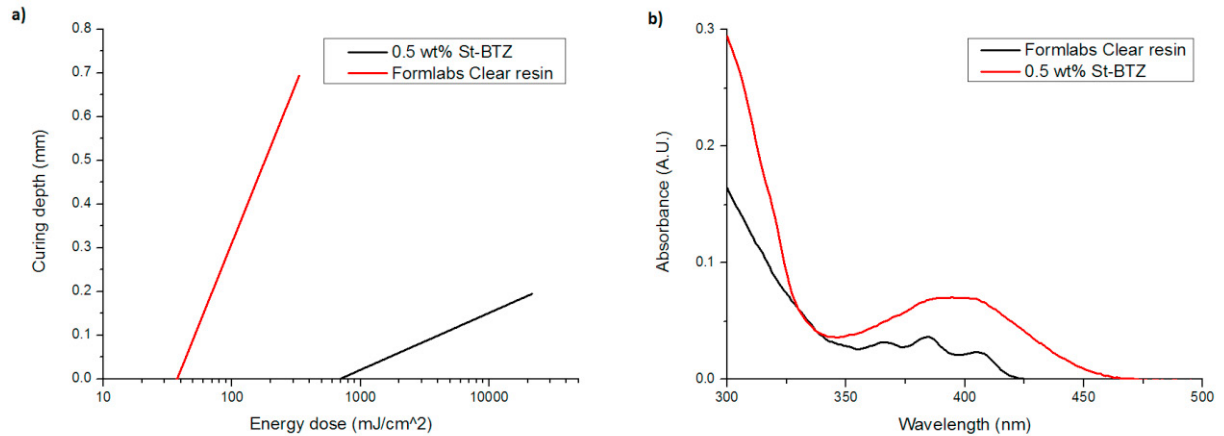


Fig. 1. a) working curve displaying measured panel thicknesses for a given energy exposure dose for curing Formlabs Clear resin with and without St-BTZ; b) liquid state UV/vis absorption spectra of Formlabs Clear resin with and without St-BTZ.

After obtaining optical properties ( $E_c$  and  $D_p$ ) of 0.5 wt% St-BTZ resin, the optimal SLA printing parameters were established (energy exposure related parameters, such as laser power and speed, scan line spacing, number of passes, etc.). These were used to successfully fabricate 0.5 wt% St-BTZ polymer structures. SEM image of 3D printed structure, with 0.5 wt% St-BTZ concentration, shows layer-by-layer fabrication nature of SLA, as illustrated in Fig. 2b. First few layers show thickness larger than indented layer thickness of 25  $\mu\text{m}$  due to higher energy dose received to improve the adhesion with the build platform. 3D printed St-BTZ-co-PMMA sample shows a broad absorption peak in the visible light region, with maximum absorbance at  $\sim 430$  nm, as shown by UV/vis absorption spectra in Fig. 2a.

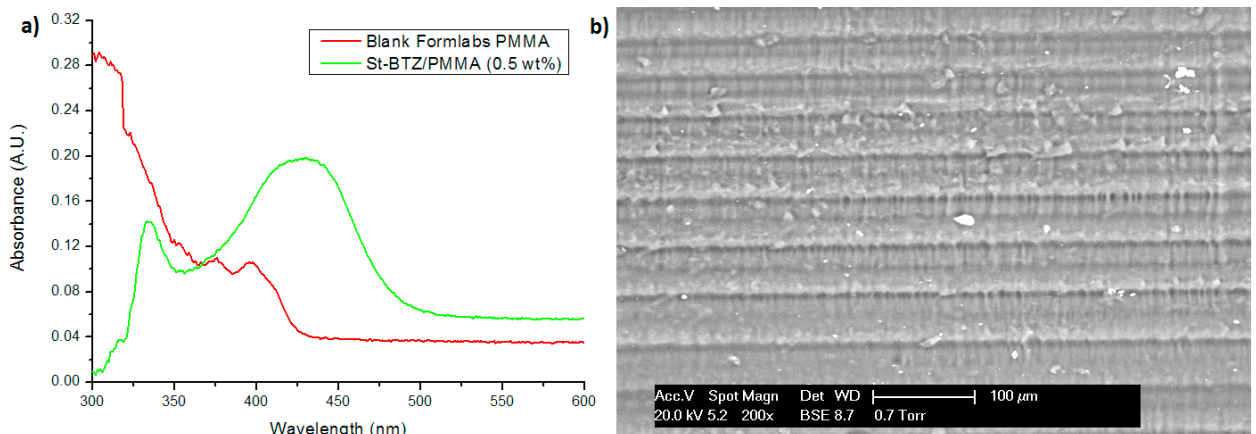


Fig. 2. a) solid state UVvis absorption spectra of 3D printed films with and without St-BTZ; b) SEM image of a 3D printed sample containing 0.5 wt% St-BTZ.

### 3.2. Photocatalytic reaction under batch conditions

Heterogeneous singlet oxygen generation in an aqueous environment was confirmed by the conversion of 2-furoic acid into 5-hydroxy-2(5H)-furanone, which was previously reported.[10] To investigate the feasibility of employing 3D printed St-BTZ-co-PMMA polymer in singlet oxygen photogeneration in water, photo-polymerized St-BTZ-co-PMMA, containing 0.5 wt% St-BTZ, was dispersed in aqueous solution of 2-furoic acid and irradiated at 420 nm for 22 hours, with oxygen bubbled at the rate of 15 mL min<sup>-1</sup>. The extent of reaction was followed by <sup>1</sup>H NMR spectroscopy, and the conversion calculated from the ratio of peaks was assigned to the starting material (2-furoic acid) and the product (5-hydroxy-2(5H)-furanone). The kinetics of reactions between <sup>1</sup>O<sub>2</sub> and the substrate, in this case 2-furoic acid, can be simplified by the pseudo-first-order model:[11]

$$\frac{C}{C_0} = e^{-kt} \quad (2)$$

where C is the concentration of the substrate (mM or mg L<sup>-1</sup>), t is the reaction time (h), and k is the pseudo-first-order rate constant (h<sup>-1</sup>) and C<sub>0</sub> is the initial concentration of the substrate. Two control experiments were performed using: (i) blank PMMA sample without any St-BTZ present under 420 nm illumination; and (ii) dark conditions (no light) in the presence of St-BTZ. No conversion of 2-furoic acid, and therefore no production of <sup>1</sup>O<sub>2</sub>, was observed after 22 hours under these two control conditions. In case of the photo-polymerized sample containing 0.5 wt% St-BTZ, ~18% conversion of 2-furoic acid, with 5-hydroxy-2(5H)-furanone being the only product was observed in <sup>1</sup>H NMR spectra after 22 hours of irradiation at 420 nm. The kinetics of 2-furoic acid conversion was fitted to the pseudo-first-order model by a non-linear regression of concentration versus time data, as shown in Fig. 3b. From this pseudo-first-order model, the pseudo-first-order rate constant was estimated to be 0.0103 h<sup>-1</sup>.

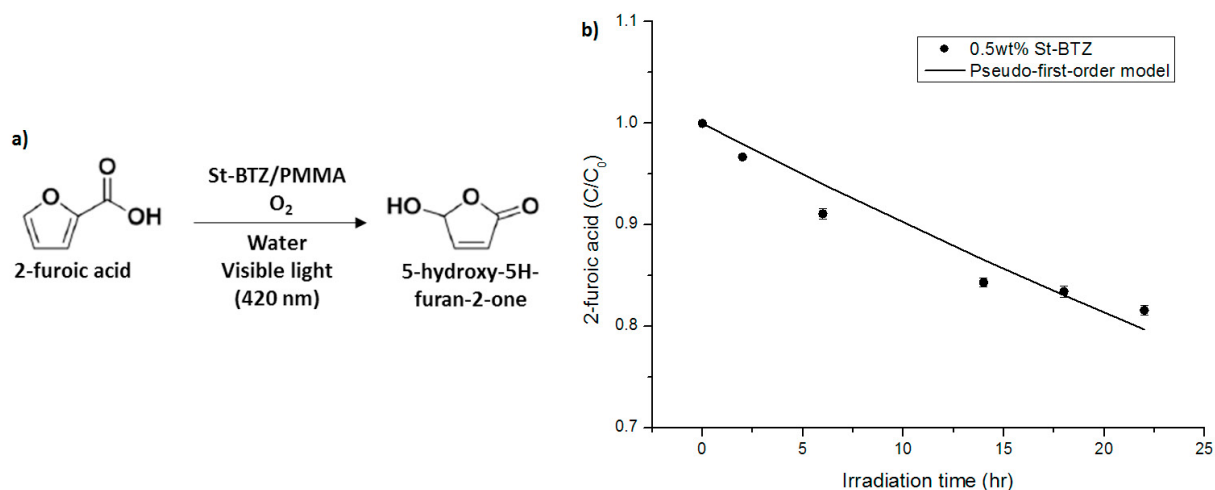


Fig. 3. a) schematic representation of conversion of 2-furoic acid into 5-hydroxy-2(5H)-furanone via the photosensitization of singlet oxygen under 420 nm light irradiation; b) conversion of 2-furoic acid into 5-hydroxy-2(5H)-furanone via photo-polymerized St-BTZ-co-PMMA, containing 0.5 wt% St-BTZ, dispersed in aqueous solution irradiated at 420 nm for 22 hours.

### 3.3. Photocatalytic reaction in flow employing 3D printed prototype

SLA was employed to directly fabricate a continuous flow photoreactor prototype, containing 0.5 wt% St-BTZ. A reactor design (Fig. 4a) with inner channel diameter of 1 mm, wall thickness of 500 μm and total volume of 0.1 ml, was successfully fabricated in a Form 1+ 3D printer, as depicted in Fig. 4b. An aqueous solution of 2-furoic acid was pumped through a 3D printed 0.5 wt% St-BTZ prototype reactor at a flowrate of 0.1 mL min<sup>-1</sup>, concurrently oxygen was pumped through a second pump at the same flow rate (0.1 mL min<sup>-1</sup>), mixing with the solution at a T junction

before entering the inlet 3D printed reactor. After irradiation of the photoreactor at 420 nm whilst cycling reaction solution for 5 hours, the conversion of 2-furoic acid was evaluated by recording  $^1\text{H}$  NMR spectra, filtering of the photosensitizer was not required, since the photo-active St-BTZ is immobilized within the reactor.  $^1\text{H}$  NMR spectra of the reaction mixture after 5 hour cycling (Fig. 4c) showed  $\sim 5.7\%$  conversion of 2-furoic acid, with 5-hydroxy-2(5H)-furanone being the only product observed. The low conversion and slow reaction rate can be explained by the use of water as a solvent, since lifetime of singlet oxygen varies considerably in different solvents, and is very short in water, compared to organic solvents. The reason behind the choice of water as the solvent in this work, is due to the fact that water is “greener solvents” compared to the more hazardous halogenated solvents. Another reason was the incompatibility of PMMA with most organic solvents. Future work will involve development of customized SLA resins for fabrication of reactors that are resistant to organic solvents.

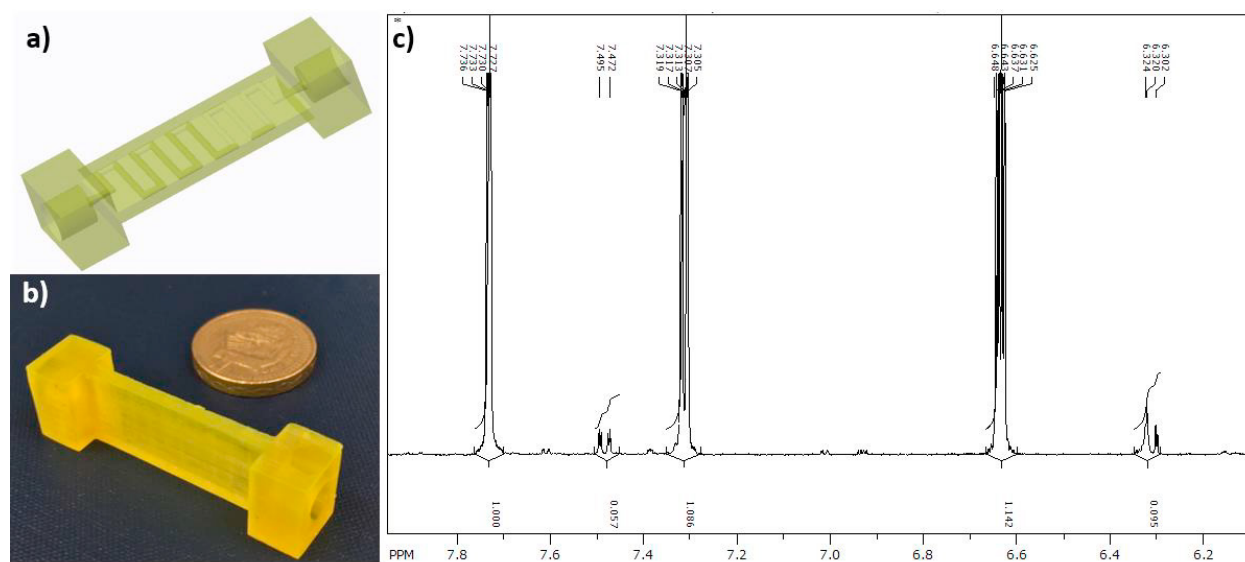


Fig. 4. a) CAD image of 0.1 ml photoreactor; b) image of a 3D printed 0.5 wt% St-BTZ 0.1 ml photoreactor; c)  $^1\text{H}$ -NMR spectra of the mixture of 2-furoic acid irradiated at 420 nm with cycling for 5 hours (NMR conversion:  $\sim 5\%$ ) in  $\text{D}_2\text{O}$ , peaks at 7.73, 7.31, 6.63 ppm attributed to 2-furoic acid, 7.48, 6.32 ppm attributed to the 5-hydroxy-2(5H)-furanone.

#### 4. Conclusion

This work provided an insight into how development of bespoke photoactive resins can enable the application of SLA in fabrication of continuous flow photoreactors, where a photo-active unit is directly incorporated within the polymer matrix. St-BTZ was successfully incorporated into a commercially available SLA resin, which was subsequently used to fabricate a 3D photosensitizing continuous flow reactor prototype for singlet oxygen generation. Results indicate that the even with small concentration of St-BTZ (0.5 wt%), SLA fabricated small scale (0.1 ml) photoactive continuous flow reactor shows activity in photosensitization of singlet oxygen synthesis under visible light irradiation (420 nm). 5.7% conversion of 2-furoic acid to 5-hydroxy-2(5H)-furanone via the photosensitization of singlet oxygen was achieved after 5 hours cycling of reaction solution. Future work will involve design and fabrication of larger volume photoreactors with intricate flow features and development of SLA resins to produce organic solvent resistant structures.

## Acknowledgements

The research work is supported by UK Engineering and Physical Science Research Council EPSRC Grant (EP/R012164/1) and Royal Society Research Grant (RSG\R1\180162).

## References

1. Lewis, N.S. and D.G. Nocera, *Powering the planet: Chemical challenges in solar energy utilization*. Proceedings of the National Academy of Sciences, 2006. **103**(43): p. 15729.
2. Ciamician, G., *THE PHOTOCHEMISTRY OF THE FUTURE*. Science, 1912. **36**(926): p. 385.
3. Wong, Y.L., et al., *Conjugated porous polymers for photocatalytic applications*. J. Mater. Chem. A, 2016. **4**(48): p. 18677-18686.
4. Tobin, J.M., et al., *Polymer-Supported Photosensitizers for Oxidative Organic Transformations in Flow and under Visible Light Irradiation*. ACS Catalysis, 2017. **7**(7): p. 4602-4612.
5. Cambié, D., et al., *Applications of Continuous-Flow Photochemistry in Organic Synthesis, Material Science, and Water Treatment*. Chemical Reviews, 2016. **116**(17): p. 10276-10341.
6. Bhattacharjee, N., et al., *The upcoming 3D-printing revolution in microfluidics*. Lab Chip, 2016. **16**(10): p. 1720-42.
7. Au, A.K., et al., *3D-Printed Microfluidics*. Angew Chem Int Ed Engl, 2016.
8. Waheed, S., et al., *3D printed microfluidic devices: enablers and barriers*. Lab on a Chip, 2016. **16**(11): p. 1993-2013.
9. Gong, H., et al., *Optical approach to resin formulation for 3D printed microfluidics*. RSC Advances, 2015. **5**(129): p. 106621-106632.
10. Urakami, H., K. Zhang, and F. Vilela, *Modification of conjugated microporous poly-benzothiadiazole for photosensitized singlet oxygen generation in water*. Chem Commun (Camb), 2013. **49**(23): p. 2353-5.
11. Tobin, J.M., et al., *BODIPY-based conjugated microporous polymers as reusable heterogeneous photosensitisers in a photochemical flow reactor*. Polym. Chem., 2016. **7**(43): p. 6662-6670.