

## Supplementary Materials for

### **Programmable photochemical deoxygenation for 2.5D grayscale printing**

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## 1. General materials

### 1.1 Chemicals

All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. The dimethyl sulfoxide (DMSO) and methylpyrrolidone (NMP) used for printing were of analytical grade. The DMSO and NMP used for photophysical measurements were of spectroscopic grade. Pentaerythritol tetraacrylate (PETA, stabilized with MEHQ, 80%) and trimethylolpropane triacrylate (TMPTA) were purchased from Innochem, Inc. and purified through a column packed with alumina (200-300 mesh, basic) to remove the stabilizer, and stored them in a refrigerator at 4 °C before conducting experiments. Pd(II) tetraphenyltetrabenzoporphyrin (PdTPBP) and Pt(II) *meso*-tetraphenyl tetrabenzoporphine (PtTPBP), Pt(II) octaethylporphyrin (PtOEP), Pt(II) (4,4'-di-tert-butyl-2,2'-bipyridine)-2(1H-benzo[de]isoquinoline-1,3(2H)-dione-2-butyl-6-ethynyl) (Pt(dbbpy)(BuNI)) were purchased from Frontier Scientific, Inc. Isopropanol used for removing redundant resin was of analytical grade.

## 2. Photophysical properties of PdTPBP

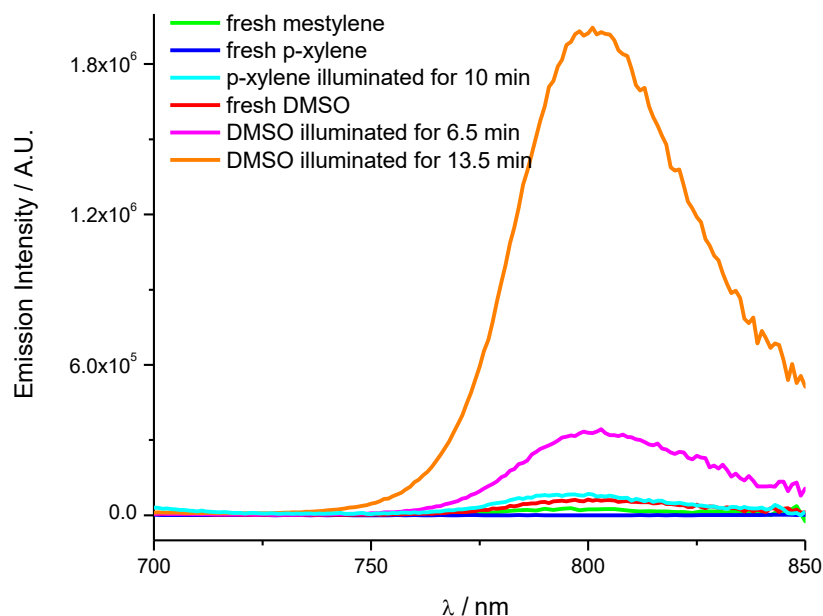
### 2.1 Molecular spectroscopy tests

UV-Vis absorption spectra were recorded on a Thermo Scientific Evolution 201 UV-Visible Spectrophotometer. Photo-emission, excitation spectra and lifetimes for solutions were recorded on Edinburg spectrometer FLS-980 equipped with a Xe light source and an MCP-PMT detector in a cooled housing (−20°C) which covers a range of 200–870 nm, and an NIR-PMT detector in a cooled housing (−80°C, cooled by liquid nitrogen) which covers a range from 600–1700 nm. Emission traces were recorded on FLS-980 (EI) by using the multiple scan mode and the shutter was set as always open. Emission intensity at fixed wavelength versus time elapsed were recorded on FLS-980 by using the kinetic scan mode and the shutter was set as always open. All the measurements have been done at room temperature (RT).

Irradiation power of Xe lamp in the FLS-980 fluorimeter and projector was measured using a ThorLabs (Newton, NJ, USA) Energy Console Meter (PM100D) equipped with a Photodiode Power Sensor, 200–1100 nm (S120VC) or a Thermal Surface Absorber Sensor, 190 nm–20 μm (S425C). Optical power of diode lasers was measured using a CNI Thermoelectric Laser Power Meter

(TS50+TP100) which covers a wavelength range of 190 nm–25  $\mu\text{m}$  (Changchun New Industries Optoelectronics Technology Co., Ltd., China).

## 2.2 Photophysical properties of PdTPBP in DMSO solution



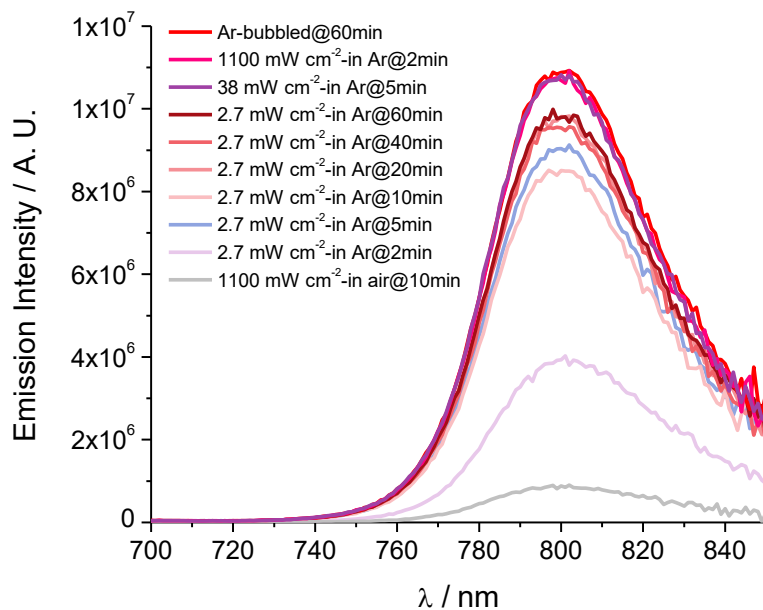
**Fig. S1** Emission spectra of PdTPBP dissolved in aerated DMSO and two control solvents of mesitylene and *p*-xylene with a concentration of  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  respectively and excited with a 635 nm xenon lamp. In mesitylene or *p*-xylene, negligible emission intensity was observed and even after 10 min illumination.

**Table R1** Photophysical properties of PdTPBP in DMSO solution after several deoxygenation methods

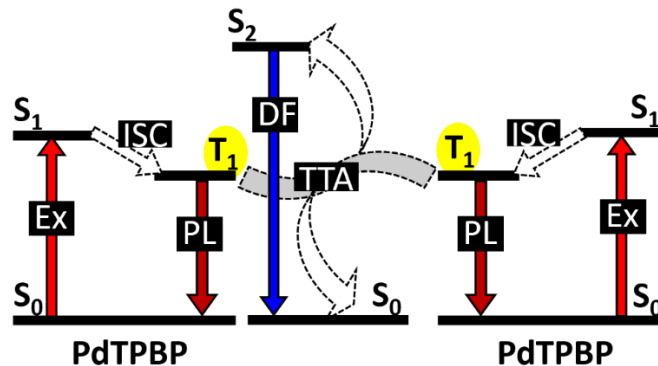
	635 nm Xenon light ( $2.7 \text{ mW cm}^{-2}$ )							635 nm laser ( $38 \text{ mW cm}^{-2}$ )	635 nm laser ( $1.1 \text{ W cm}^{-2}$ )	Argon bubbled
	Time (min)	0	2	5	10	20	40	60	5	2
Photon counts at 798 nm ( $\times 10^{-7}$ )	\	0.39	0.90	0.85	0.97	0.95	1.0	1.1	1.1	1.1
$\Phi$	0.01	0.03	0.07	0.07	0.10	0.11	0.12	0.13	0.13	0.13
$\tau/\mu\text{s}$	\	70	152	214	223	228	240	266	262	250

It's noteworthy that, if the upper air was not removed, even with sealing, after 10 minutes of illumination with a light intensity of  $1.1 \text{ W cm}^{-2}$ , the quantum yield was 0.03, and the lifetimes were 8.2 s and 42 s. This was considered as the rapid diffusion of atmospheric oxygen into the deoxygenated solution, therefore, all experiments were conducted using cuvettes equipped with

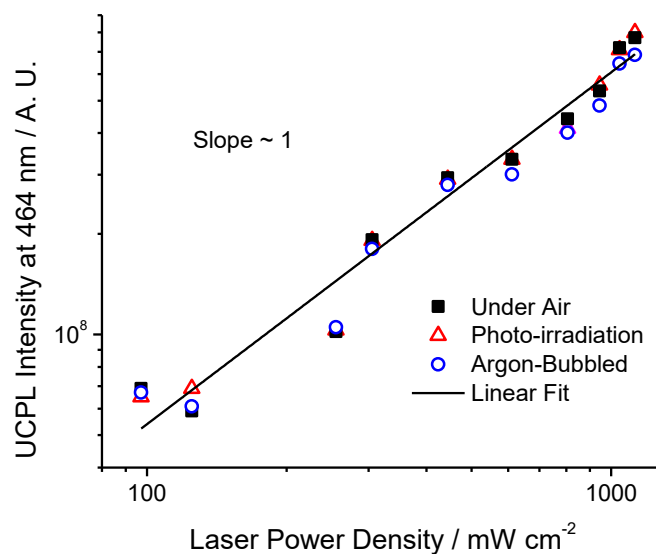
extended handles, and the upper air was removed with argon for 5 minutes.



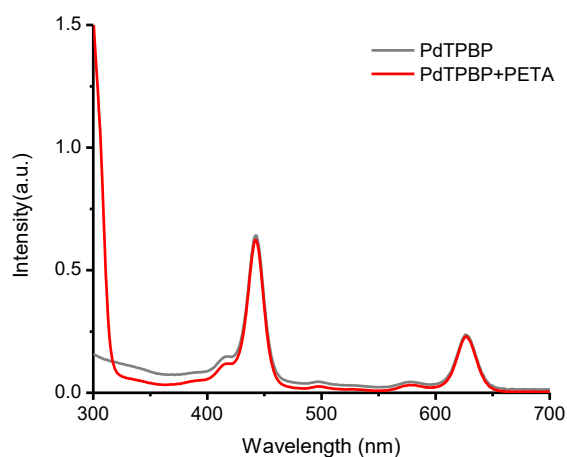
**Fig. S2** Emission traces of various DMSO solutions containing  $1 \times 10^{-5} \text{ mol dm}^{-3}$  PdTPBP upon argon bubbled for 60 min or irradiation with a 635 nm laser over time at 298 K.



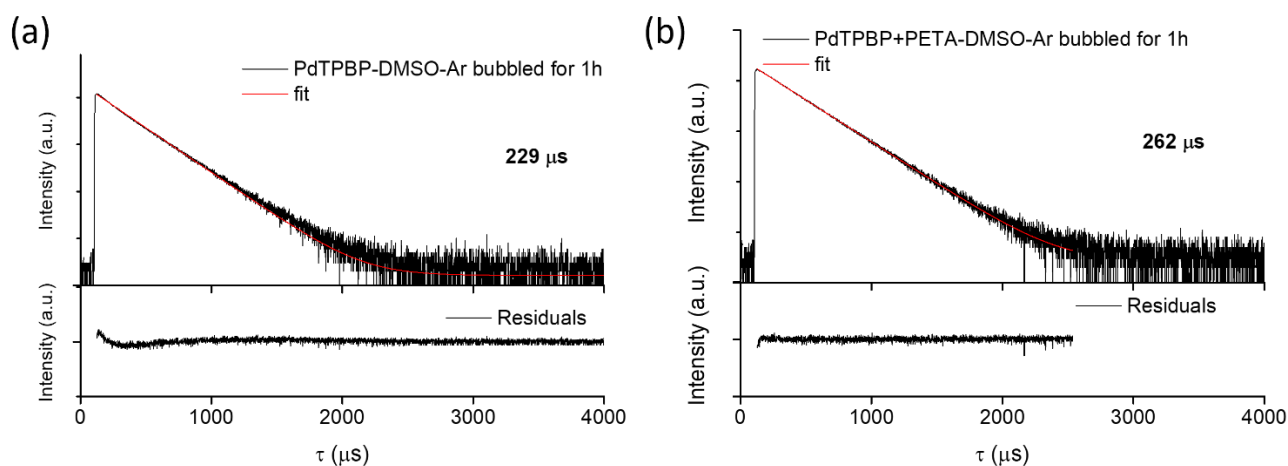
**Fig. S3** The Jablonski diagram of homomolecular triplet-triplet annihilation upconversion (TTA-UC) for PdTPBP was illustrated based on the absorption and emission spectra recorded in a DMSO solution.



**Fig. S4** Double logarithmic plots of the upconverted fluorescence intensity at 464 nm against laser OPD under different conditions.



**Fig. S5** UV-Vis absorption spectra of a mixture of PdTPBP ( $1.0 \times 10^{-5}$  mol dm<sup>-3</sup>) and PETA (0.5 mol dm<sup>-3</sup>) in aerated DMSO. The addition of PETA into the solution of PdTPBP did not induce substantial changes in the absorption spectrum of PdTPBP. The absence of any alteration in this absorption profile suggested the absence of ground-state complexation between PdTPBP and PETA.

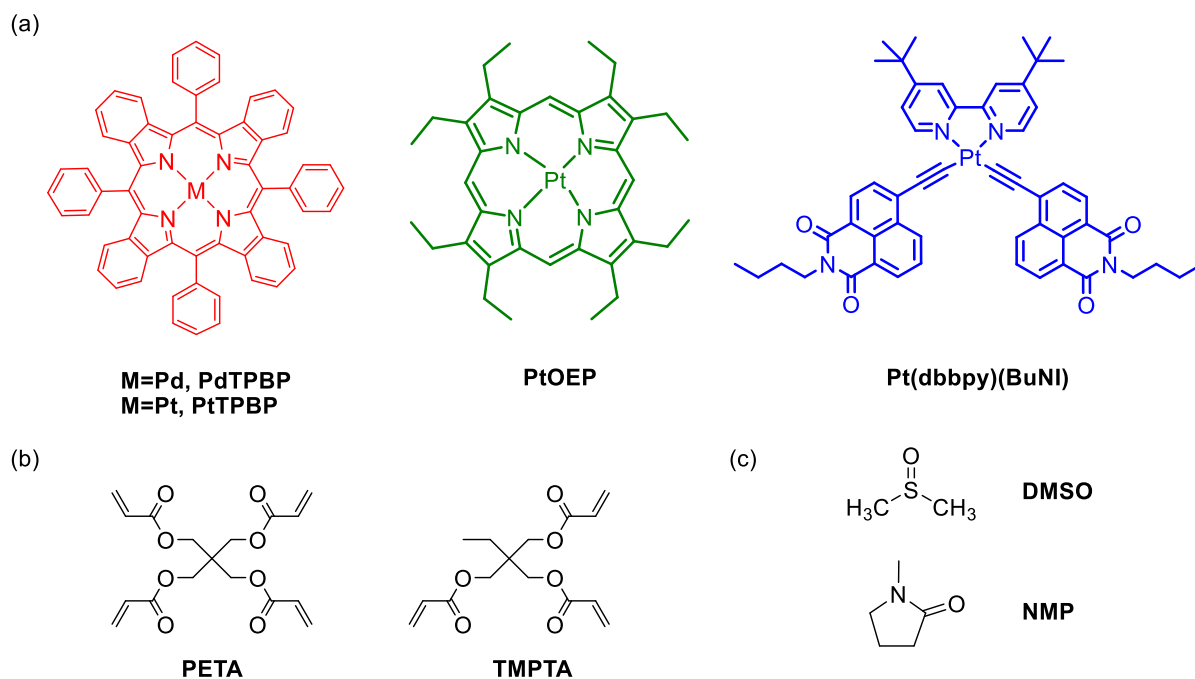


**Fig. S6** (a) Lifetimes recorded for  $1 \times 10^{-5} \text{ mol dm}^{-3}$  PdTPBP in DMSO solution (bubbled with argon for one hour) under 450 nm excitation and detected at 798 nm, obeying first-order kinetics with long-lived phosphorescence. (b) Lifetimes recorded for  $1 \times 10^{-5} \text{ mol dm}^{-3}$  PdTPBP after addition of  $1 \text{ mol dm}^{-3}$  PETA in DMSO solution (bubbled with argon for one hour) under 450 nm excitation. The decay curves of  $^3\text{PdTPBP}^*$  measured at 798 nm displayed an increase in the lifetime of  $^3\text{PdTPBP}^*$  as more PETA was added, indicative of an anti-quenching process. This observation can be attributed, in part, to the varying solubility of oxygen as a function of the sample composition.

### 3. Polymerization dynamics of PtTPBP and PdTPBP

#### 3.1 Photosensitizers for polymerization

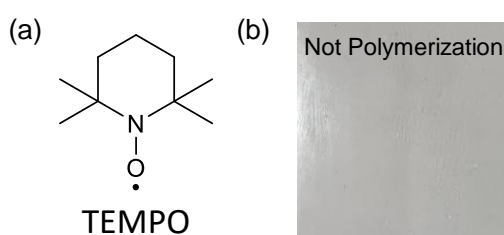
Preliminary experiments were conducted and found that any combination of different phosphors with distinct absorption properties, different monomers, and various deoxygenating solvents can undergo curing under their respective excitation lights. PdTPBP was chosen as a red-to-blue upconversion photosensitizer when compared to PtTPBP because its longer lifetime induced longer time to deoxygenate which made room for the control of initiating and inhibiting in the printing process.



**Fig. S7** (a) Phosphors excited at 635 nm, 532 nm, and 445 nm respectively. (b) Monomers with four and three functionalities. (c) Deoxygenating solvents for photopolymerization

### 3.2 Polymerization mechanism

We added 0.02 wt% of the free radical inhibitor 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) to the resin solution containing PdTPBP ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ), PETA ( $2.7 \text{ mol dm}^{-3}$ ) and DMSO and observed that after 25 minutes of illumination, solidification did not occur, providing confirmation of the radical polymerization mechanism.



**Fig. S8** (a) Chemical structure of TEMPO. (b) The after-print glass plate with the addition of 0.02 wt% of the radical inhibitor TEMPO.

### 3.3 Fourier transform infrared spectroscopy (FT-IR) of PdTPBP

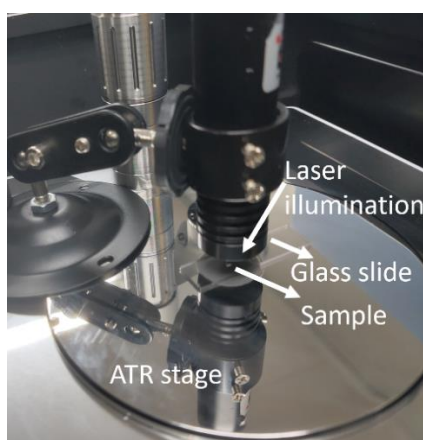
Our methodology mainly draws upon the works from Prof. Castellano<sup>[1]</sup> and Prof. Hayward<sup>[2]</sup>. Attenuated total reflection fourier transform infrared spectra (ATR-IR) was used to monitor the conversion of acrylate monomers over time. Measurements were performed by preparing the resin as

for photopolymerization and placing 25  $\mu\text{L}$  resin on the ATR window and covering a glass plate to form a thin layer free of bubbles. A 635 nm diode laser with a linear-shape were aimed at the sample and the light intensity at the sample plane was measured with the power meter before polymerization. The experimental setup is shown in Figure S9. Each measurement started with no illumination for 30 s to establish an initial area under the curve, after which the light was turned on to observe polymerization over time at various resin formulations and light intensities. Polymerization was monitored by observing the disappearance of the  $=\text{CH}_2$  acrylate peak at  $810\text{ cm}^{-1}$ .<sup>[ref]</sup> Peak areas were integrated of the wavenumbers between  $795\text{ cm}^{-1}$  and  $817\text{ cm}^{-1}$  using the software OPUS 8.5. The peak of the carbonyl group at  $1720\text{ cm}^{-1}$  was recognised as the internal standard for normalization because it was not affected during the curing process. Conversion over time was calculated by comparing the signal to the initial area under the curve before turning on the light, as follows:

$$\text{conversion} = \frac{A_{t_0} - A_{t_i}}{A_{t_0}},$$

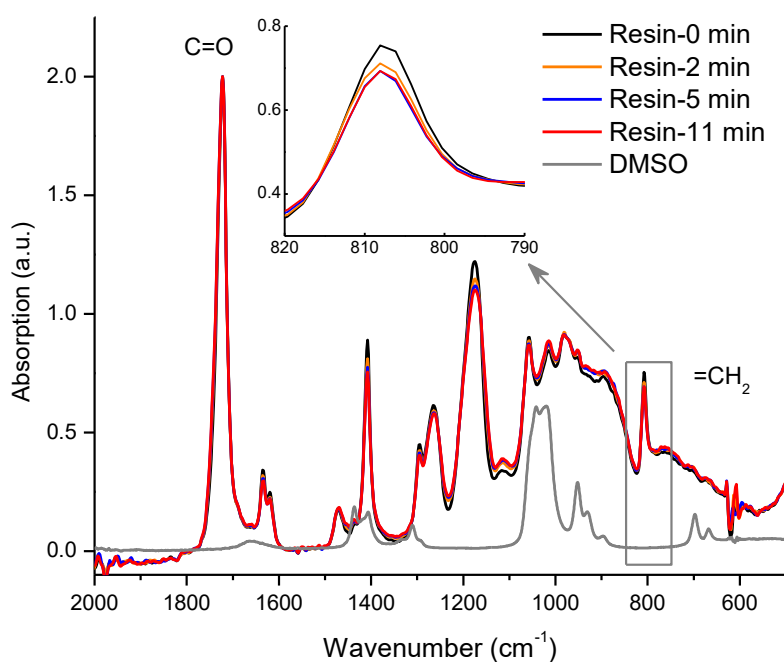
where  $A_{t_0}$  is the initial integral area in dark,  $A_{t_i}$  is the  $=\text{CH}_2$  bonds absorption area at the  $i$  exposure time.

An example graph of conversion over time and the conversion rate calculation is shown in Figure S7. Exponential fits were conducted for all curves of conversion over time using the function ‘Asymptotic1’ in the software OriginPro 2016.



**Fig. S9** Set-up for ATR-IR measurements under 635 nm laser illumination in air.





**Fig. S10** Selected plots for illustration the conversion over time of =CH<sub>2</sub> under continuous illumination using C=O as an internal standard. Resin containing PdTPBP ( $1 \times 10^{-4}$  mol dm<sup>-3</sup>), PETA ( $2.7$  mol dm<sup>-3</sup>) and DMSO.

#### 4. Profilometry of gradient structures

##### 4.1 Optical power density testing

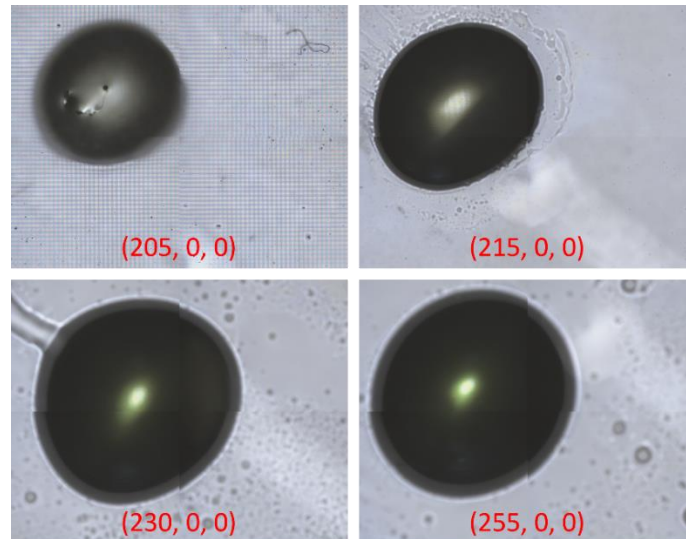
The BenQ MH741 (1920×1080 dpi) projector was placed 9 cm away from the centre of the imaging chamber. PowerPoint was used to draw the 5x5 cm<sup>2</sup> square and projected the images. Change the red channel in the RGB values in turn. Measure and plot the relationship between optical power density and RGB values.

##### 4.2 Thickness and diameter measurements

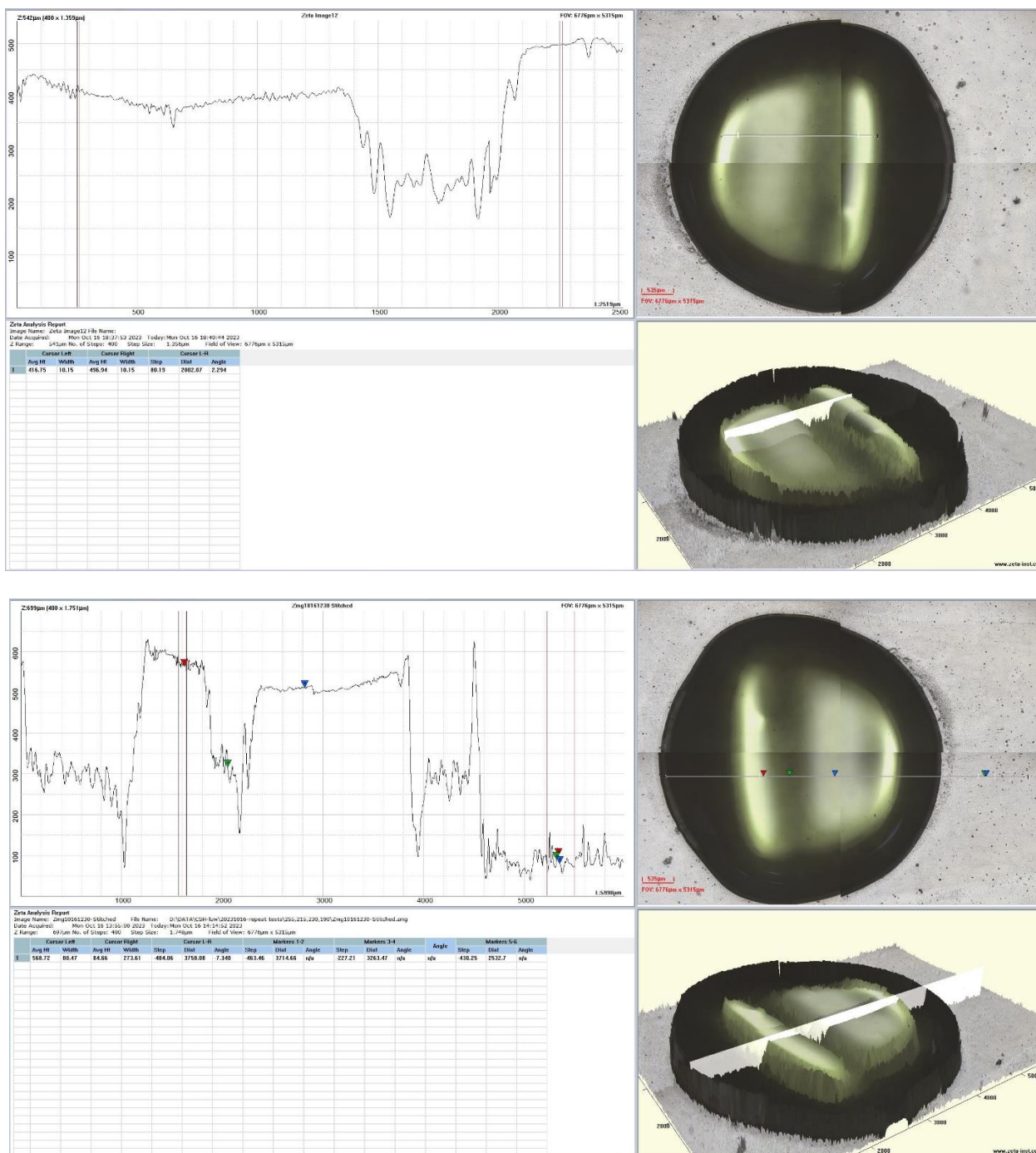
A circle with a diameter of 5 mm was projected and used as the incident pattern. A DMSO solution of PdTPBP ( $1 \times 10^{-4}$  mol dm<sup>-3</sup>) and PETA ( $2.7$  mol dm<sup>-3</sup>) was prepared and loaded in the imaging chamber. The glass pieces were sonicated in isopropyl alcohol solution for 20 min and dried naturally. After 25 min continuous irradiation, immerse the glass sheet in isopropyl alcohol solution to remove the uncured liquid. Hemispheres can be observed and characterized using an optical

profiler. Circle patterns with different red value were projected from top to bottom into the resin tank covered with glass sheets for 25 minutes. The cured hemispheres would adhere to the glass sheets, and the residual uncured resin was removed by immersing in isopropanol solution.

Optical profilometry measurements were conducted in ZETA-20 (purchased from KLA Company).



**Fig. S11** Optical profilometry for four grayscale hemispheres after printing and their 2D stitched images.

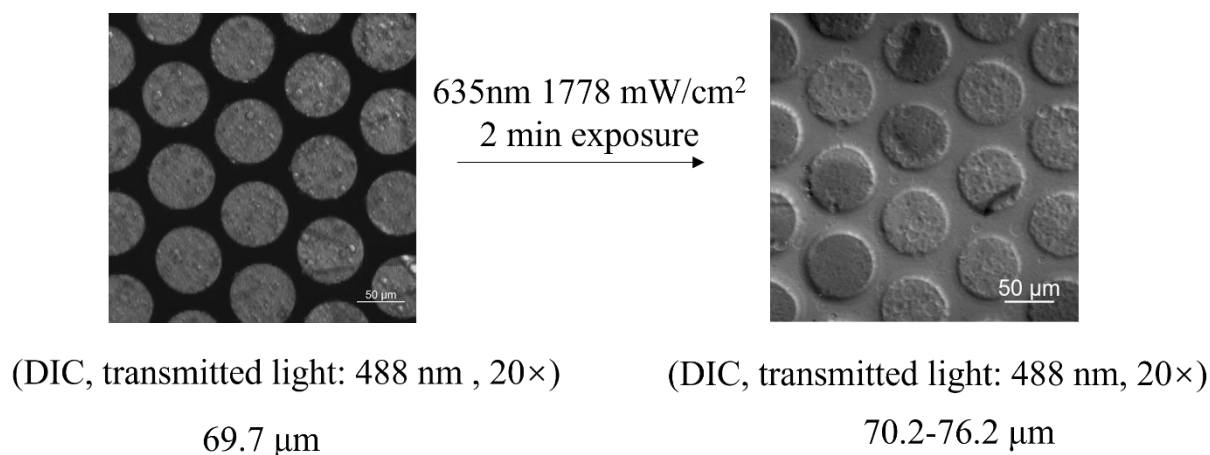


**Fig. S12** Thickness profiles extracted along three horizontal dividing lines. 3D thickness profile was provided as well (bottom-right).

### 4.3 2D microfabrication

Using a confocal laser scanning microscope (Zessiss, LM900) equipped with a low-energy light source, we patterned a micron-sized object. As a proof-of-concept, a mixture of PdTPBP ( $5 \times 10^{-5}$  mol

dm<sup>-3</sup>) in PETA (3.06 mol dm<sup>-3</sup>) and DMSO was illuminated through a photo-mask (a TEM grid) for 2-min of exposure, using a 635 nm laser (1778 mW cm<sup>-2</sup>) in order to selectively excite the Q-band of PdTPBP. The in situ bright-field images generated with a 488 nm Ar<sup>+</sup> laser line to avoid exciting the initiator features, a well-defined two-dimensional grid patterns obtained with a diameter of 70  $\mu$ m.



**Fig. S13** Images of a micron-sized polymer gel captured using a confocal laser scanning fluorescence microscope.

## 5 Grayscale 2.5D printing

### 5.1 Grayscale patterns design

Grayscale images obtained from online were converted into RGB images with only the red channel using the provided code. The purpose of this code is to convert a given original image into a solid red image. It achieves this by setting the values of the green and blue colour channels to 0 for each pixel, while retaining the value of the red channel, effectively converting the original image into a red-only image.

```
import cv2
from PIL import Image

def color2red(color_img):
    """
    function: transform original image to grayscale image with red channel only.
    :param color_img: the original image
    :return: the red image
```

```

'''
size_h, size_w, channel = color_img.shape
for i in range(size_h):
    for j in range(size_w):
        color_img[i,j,1] = 0
        color_img[i,j,2] = 0
return color_img

if __name__ == '__main__':
    dir_ori_image = 'C:/ Desktop/b.jfif' # file path of the original image
    dir_save_image = "C:/ Desktop/reda.jfif" # file path to save resulted image
    pic = cv2.imread(dir_ori_image)
    pic_red = color2red(pic)
    im = Image.fromarray(pic_red)
    im.save(dir_save_image)
    print(pic_red)
'''

```

(0, 0, 0)

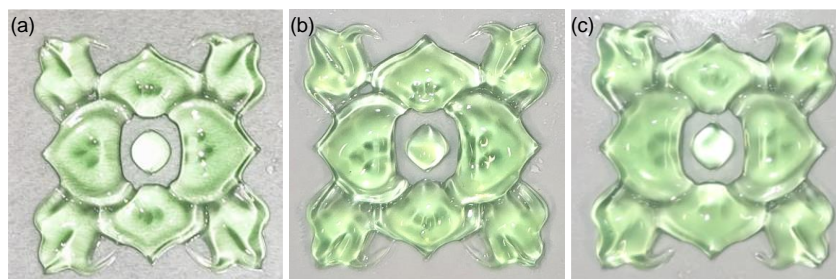
Red light in grayscale

(255, 0, 0)

**Fig. S14** Code for converting grayscale image into solid red image and corresponding red channel in RGB color mode.

## 5.2 Grayscale 2.5D printing

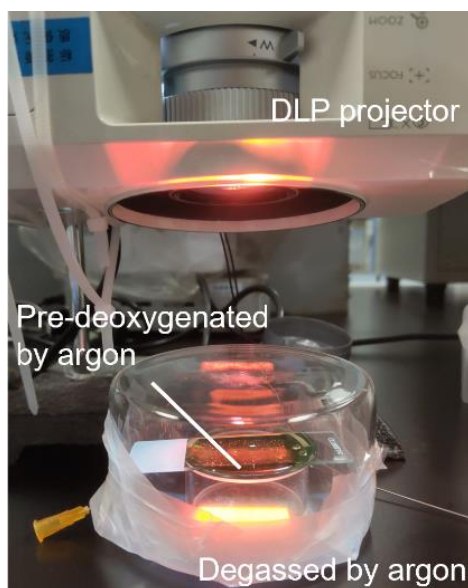
A DMSO solution of PdTPBP ( $1 \times 10^{-4}$  mol dm<sup>-3</sup>) and PETA (2.7 mol dm<sup>-3</sup>) was prepared and loaded in the imaging chamber. The BenQ MH741 projector (1920×1080dpi) was placed 9 cm away from the center of the imaging chamber. PowerPoint was used to draw the figures and project the images. The color of the figures and the background of PowerPoint slides was set as red (650 nm, RGB (R, 0, 0)) and black, respectively.



**Fig. S15** Comparison of grayscale flower patterns after three separate printings.

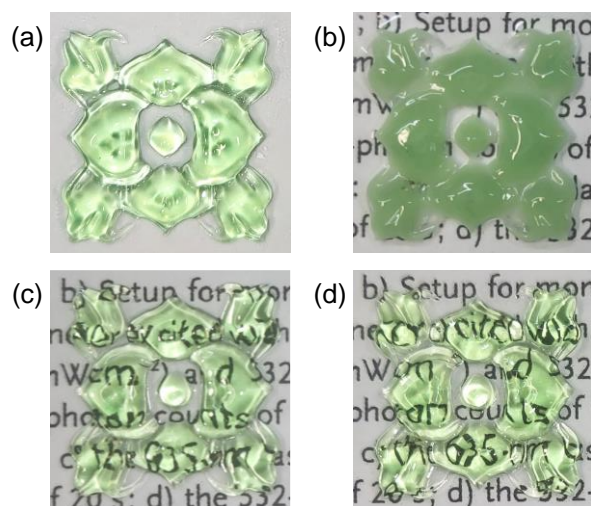
### 5.3 Oxygen-free device

Experiments were conducted under oxygen-free conditions. The resin was purged with argon for over an hour to eliminate oxygen and subsequently printed under an argon atmosphere.



**Fig. S16** Device for grayscale printing under argon atmosphere.

### 5.4 Solvent displacement experiments



**Fig. S17** Grayscale pattern after several processing procedures: (a) as-printed pattern, (b) water-soaking for 19 h, (c) vacuum dry at 80 °C for 3 h, (d) vacuum dry at 80 °C for another 4 h.