Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering. This journal is © The Royal Society of Chemistry 2022

# **Supporting Information for**

# 4D Printing of Light Activated Shape Memory Polymers with Organic Dyes

Matteo Gastaldi,<sup>‡,a</sup> Christoph A. Spiegel,<sup>‡,b,c</sup> Clara Vazquez-Martel,<sup>‡,b,c</sup> Claudia Barolo,<sup>a,d</sup> Ignazio Roppolo, \*<sup>e</sup> Eva Blasco \*<sup>b,c</sup>

<sup>a</sup>Department of Chemistry and NIS Interdepartmental Centre and INSTM Reference Centre, University of Torino, Via Pietro Giuria 7, 10125 Torino, Italy

<sup>b</sup>Institute of Organic Chemistry, Heidelberg University, Heidelberg 69120, Germany

<sup>c</sup>Institute for Molecular Systems Engineering and Advanced Materials, Heidelberg University, Im Neuenheimer Feld 225, 69120 Heidelberg, Germany

<sup>d</sup>ICxT Interdepartmental Center, University of Turin, Lungo Dora Siena 100, 10153 Torino, Italy

<sup>e</sup>Department of Applied Science and Technology, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129, Turin, Italy

**‡** These authors contributed equally.

\* Corresponding Authors: <u>eva.blasco@oci.uni-heidelberg.de</u>; <u>ignazio.roppolo@polito.it</u>

This document contains 23 pages (including this cover sheet), 1 Scheme, 17 Figures and 3 Tables

#### TABLE OF CONTENT: ADDITIONAL IMAGES AND DATA

# Materials & InstrumentationPage 3 - 4Synthesis of Acrylate Photopolymerizable Azo-dyesPage 5 - 12Scheme S1. Synthetical pathway to obtain push-pull azo-dyes (top) and acrylate photopolymerizable azo-<br/>dyes (bottom).Figure S1 - S5. NMR of all synthesized compounds.

#### UV-Vis Analysis of Acrylate Photopolymerizable Azo-dyes

**Figure S6.** UV-Vis spectra of the four synthesized azo-dyes. The spectra were measured in XYZ, alone as well as together with the used photoinitiator BAPO with a concentration of XYZ.

#### DLP 3D Printing: Formulation and Printing Parameter Studies

**Table S1.** Evaluation of the optimal concentration of the chlorine azo-dye compound in the liquid formulation. The LED irradiation time is the time required to complete the photopolymerization process under 380-390 nm UV light.

**Figure S7.** Working curves for the inks including 2 wt % BAPO and 0.1 wt.% of the azo-dye compounds. A "blank" formulation (= no azo-dye) was studied as well for comparison.

**Table S2.** Overview of the optimized 3D printing parameters as well as the obtained photonic parameters for the inks studied containing 2 wt % BAPO and 0.1 wt.% of azo-dye compound. A "blank" formulation (= no azo-dye) was studied as well for comparison.

#### FTIR-analysis

Figure S8. FTIR spectra of the AzoCI-based ink and a printed structure before and after recovery.

**Figure S9.** Section of the FTIR spectra of a) the AzoCl based ink and b) the corresponding 3D printed polymer used for the DOC calculation. Signals at 809 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> correspond to the double-bond band of the acrylate group and the band of the carbonyl group, respectively.

#### Analysis of the xy-resolution of the printed samples

**Figure S10.** Analysis of the xy-resolution of the printed samples. Schematic representation of the test specimen geometry consisting of engraved line gratings with varying period and width is given in (a), where t is the thickness, h the depth and d the distance between the printed lines. Measured XY plane resolution of (b) blank formulation compared to (c - f) the formulations containing the azo-dyes.

#### Characterization of the 3D Printed Shape Memory Polymers (SMPs)

Figure S11. DMA thermograms for all 3D printed samples. a) blank, b) H, c) Cl, d) OCH3, e) NO2.

Table S3. Glass transition temperatures Tg for all the 3D printed samples calculated via DMA.

Figure S12. TGA thermograms for all 3D printed samples. a) Blank, b) H, c) Cl, d) OCH3, e) NO2.

**Figure S13.** DMA analysis under LED irradiation with an increasing current (A) of the LED power supply for 3D printed polymeric samples of a) blank formulation or containing compounds b) H, c) Cl, d) OCH3, e) NO2. **Figure S14.** Calculation of the parameter a for different 3D printed structures.

**Figure S15.** Shape-memory recovery of 3D printed (a) rectangular strips, (b) frames and (c) rings under LED irradiation for all azo-dye-based formulations.

**Figure S16.** Demonstration of the photothermal response of the fabricated 3D printed samples. Surface temperature of a 3D printed blank sample (without azo-dye) and a sample containing AzoCl before and after 10 s of laser irradiation. The measurement was performed at three different laser intensities: 1 %, 3 % and 5 % (approx. 99 mW cm<sup>-2</sup>, 344 mW cm<sup>-2</sup> and 567 mW cm<sup>-2</sup>).

**Figure S17.** Demonstration of the thermal stability of the programmed shape over time at room temperature. Scale bar = 10 mm.

Page 15 - 16

Page 16 – 17

Page 18 – 22

Page 13

Page 14 – 15

# <u>Materials</u>

All reagents were purchase from Fluka and Sigma-Aldrich; unless otherwise noted, the reagents were used without any purification procedures. **1** was obtained from Fluka and used as received. All solvents were purchase from VWR and Sigma-Aldrich. Bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (BAPO), tricyclo[5.2.1.02,6]decanedimethanol diacrylate (TCDMDA), poly(ethylene glycol) diacrylate (PEGDA, average Mn 575), isobornyl acrylate (IBA) and hexyl acrylate (HA) were purchased from Sigma-Aldrich and used as received.

# Instrumentation

<sup>1</sup><u>H NMR</u> spectra were recorded on a JEOL ECZR600 FT NMR spectrometer (<sup>1</sup>H operating frequency 600 MHz). <sup>1</sup>H chemical shifts are reported relative to TMS ( $\delta$  = 0) and referenced against solvent residual peaks. Chloroform-d (Sigma-Aldrich, 99.8 atom%) or dimethyl sulfoxide-d<sub>6</sub> (Sigma-Aldrich, 99.95 atom%) was employed as deuterated solvent (CDCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H NMR, DMSO-*d*<sub>6</sub>: 2.50 ppm for <sup>1</sup>H NMR).

<u>DLP 3D Printing</u> was carried out by using a modified commercial Asiga MAX X27 UV DLP 3D printer with a LED light source of 385 nm. The printer offers a pixel resolution of 27  $\mu$ m. A custom ink vat and building platform were used to reduce ink usage during printing. The custom-made, aluminium build platform had a 25 × 25 mm2 build area. For tray modification, an aluminium inlet was placed inside a commercial tray. Successively, the space between tray walls and aluminium inlet was filled with Sylgard 184 silicone elastomer and cured at rt for 24 h. For printing, STL files of all fabricated geometries were sliced with layer thicknesses of 50  $\mu$ m and 100  $\mu$ m using the software provided by the printer. The prints were performed at room temperature. After printing, the excess ink was drained from the parts and platform and reused. Then, structures were developed and sonicated for 5 minutes twice in isopropanol and successively dried. Finally, the structures were post-cured utilizing a Asiga Flash UV chamber. Post-curing time was chosen individually depending on the geometry type.

<u>UV/Vis</u> Absorption spectra were recorded with a Shimadzu UV-1900i UV-Vis Spectrophotometer, using a resolution of 0.5 nm.

<u>Fourier transform infrared spectrometry (FTIR)</u> analysis was conducted on a JASCO FT/IR-4600 FT-IR spectrometer.

<u>Thermal gravimetric analyses (TGA)</u> were carried out with a Q600 (TA Instrument) on the polymeric samples heating from 30 °C to 700 °C with a heating rate of 10 °C/min.

Dynamic mechanical analysis (DMA) was used to evaluate the thermomechanical properties of the printed materials. 3D printed strips were prepared (29.40 mm length, 7.83 mm width and

0.90 mm thickness) and tested using a Triton Technology TTDMA. The response of the samples was observed in the temperature range of 0 °C to 110 °C with a heating rate of 3 °C min<sup>-1</sup> and a frequency of 1 Hz. For the opto-mechanical characterization, the DMA measurements were conducted under irradiation at 459 nm.

<u>Digital microscope</u> images of the samples were taken with a high-resolution digital microscope ZEISS Smartzoom 5 by using a ZEISS objective PlanApo D 1.6 x/0.1 FWD 36 mm.

<u>3D scans</u> of the printed structures were recorded with a a E4 3D scanner (3Shape) with scanning accuracy of 4  $\mu$ m.

Infrared imaging was performed by Optris PI 640i infrared thermal imaging camera.

#### Synthesis of Acrylate Photopolymerizable Azo-dyes



**Scheme S1.** Synthetical pathway to obtain push-pull azo-dyes (top) and acrylate photopolymerizable azo-dyes (bottom).

**Compound 1** is commercially available and was obtained from Sigma-Aldrich and used without further purifications.

**Compound 2** was synthesized according to the reported procedure.<sup>1</sup> Results of the characterizations are in agreement with the reported data Yield 85%.

<sup>1</sup>*H* NMR (600 MHz, Chloroform-d, **Figure S1**)  $\delta$  8.40 (d, J = 2.4 Hz, 1H), 8.16 (dd, J = 8.9, 2.4 Hz, 1H), 7.95 (d, J = 9.2 Hz, 2H), 7.78 (d, J = 8.9 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 3.91 (t, J = 5.8 Hz, 2H), 3.64 (t, J = 5.9 Hz, 2H), 3.59 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).



Figure S1. <sup>1</sup>H-NMR spectrum of compound 2 (600 MHz, Chloroform-d).

**Compound 3** was synthesized according to the following procedure (see **Scheme S1**). Aniline (0.500 g, 2.97 mmol, 1 eq) was dissolved in 50 ml of a solution of  $H_2O/CH_3COOH$  (1:4) under stirring in a round bottom flask. The mixture was put in an ice bath and the temperature was monitored to reach 0-5°C. NaNO<sub>2</sub> (0.225 g, 3.27 mmol, 1.1 eq) was dissolved in deionized 10 mL of  $H_2O$ , brought to 0-5°C and then added to the solution dropwise. After 30 minutes, the 2-(N-ethylanilino)ethanol (0.577 mL, 3.564 mmol, 1.2 eq) was suspended in 5 mL of  $H_2O$  and 1 mL of methanol was added to enhance the solubility: this solution was added dropwise to the aniline solution under vigorous stirring. The reaction was left for 3 h and then was poured in crushed ice to obtain a red precipitate that was filtered, washed with cold water and dried. Yield 93% (0.950 g, 2.76 mmol).

<sup>1</sup>*H*-*NMR* (600 MHz, Chloroform-d, **Figure S2**)  $\delta$  7.92 – 7.86 (m, 4H), 7.71 – 7.66 (m, 1H), 6.79 (d, J = 9.3 Hz, 2H), 4.08 (s, 3H), 3.89 (t, J = 5.9 Hz, 2H), 3.61 (t, J = 5.9 Hz, 2H), 3.56 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

λ<sub>max</sub> (EtOH): 490 nm

ε (L mol<sup>-1</sup> cm<sup>-1</sup>): 30.5 x 10<sup>3</sup>

HRMS: calculated 344.1485, found 345.1557 (M+1)



Figure S2. <sup>1</sup>H-NMR spectrum of compound 3 (600 MHz, Chloroform-d).

**Compound 4** was synthesized according to the procedure described by Schab-Balcerzak et al.<sup>2</sup> and all characterizations are in agreement with the reported data (Yield: 38%).

<sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ , **Figure S3**)  $\delta$  8.86 (d, J = 2.5 Hz, 1H), 8.51 (dd, J = 9.0, 2.5 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 9.3 Hz, 2H), 6.93 (d, J = 9.4 Hz, 2H), 4.89 (t, J = 5.3 Hz, 1H), 3.67 – 3.52 (m, 6H), 1.17 (t, J = 7.1 Hz, 3H).



*Figure S3.* <sup>1</sup>*H*-*NMR spectrum of compound 4 (600 MHz, DMSO-d)* 

Acrylate azo-dyes AzoH and AzoCl were synthesized following the reported procedure<sup>3,4</sup> and their characterization is in agreement with reported data. Yield Azo H 92%, Azo Cl 90%.

**AzoH:** <sup>1</sup>*H* NMR (600 MHz, Chloroform-d, **Figure S4a**) δ 8.33 (d, J = 9.1 Hz, 2H), 7.96 (d, J = 9.0 Hz, 4H), 6.84 (d, J = 9.3 Hz, 2H), 6.42 (dd, J = 17.3, 1.3 Hz, 1H), 6.12 (dd, J = 17.3, 10.5 Hz, 1H), 5.87 (dd, J = 10.5, 1.3 Hz, 1H), 4.40 (t, J = 6.3 Hz, 2H), 3.75 (t, J = 6.3 Hz, 2H), 3.57 (q, J = 7.1 Hz, 2H), 1.28 (s, 3H).

**AzoCl:** <sup>1</sup>*H* NMR (600 MHz, Chloroform-d, **Figure S4b**)  $\delta$  8.39 (d, J = 2.4 Hz, 1H), 8.15 (dd, J = 8.9, 2.4 Hz, 1H), 7.95 (d, J = 9.2 Hz, 2H), 7.78 (d, J = 8.9 Hz, 1H), 6.83 (d, J = 9.2 Hz, 2H), 6.42 (dd, J = 17.3, 1.1 Hz, 1H), 6.13 (dd, J = 17.3, 10.5 Hz, 1H), 5.87 (dd, J = 10.5, 1.1 Hz, 1H), 4.39 (t, J = 6.3 Hz, 2H), 3.74 (t, J = 6.3 Hz, 2H), 3.56 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).



*Figure S4.* <sup>1</sup>*H-NMR* spectra of *a) AzoH* and *b) AzoCl* (600 MHz, Chloroform-d).

Acrylate azo-dyes AzoOCH<sub>3</sub> and AzoNO<sub>2</sub> were synthesized according to the following procedure. **3** (0.500 g, 1.45 mmol, 1 eq) or **4** (0.500 g, 1.39 mmol, 1 eq) was put in a dried round bottom flask under inert Argon atmosphere and completely dissolved with anhydrous tetrahydrofuran under stirring. The flask was put in an ice bath and 1.1 eq (1.60 mmol, 0.223 mL for compound **3**; 1.53 mmol, 0.213 mL for compound **4**) of triethylamine was added. Then, 1.2 eq of fresh distilled acryloyl chloride (1.73 mmol, 0.141 mL for compound **3**; 1.67 mmol, 0.136 mL for compound **4**) was added dropwise over 15 minutes and after 30 minutes from the last addition the ice bath was removed and the reaction was left for 24 h, while monitoring it with TLC (Petroleum ether/Ethyl acetate 1:1). When the reaction was completed, the solution was filtered, the filter was washed with ethyl acetate to recover the desired product and the solvents were removed under vacuum at a temperature below 30°C.

The solid was dissolved with ethyl acetate, put in a separation funnel, and extracted 3 times with water and 2 times with brine. The product that remains in the aqueous fractions was extracted again with 3 times with ethyl acetate until the aqueous solution became clear.

The organic fractions were combined, dried over sodium sulphate, filtered and the solvent was removed under vacuum at 30°C. The final product was obtained as a dark red solid. Yields: **AzoOCH<sub>3</sub>** 92% (0.5311 g, 1.334 mmol), **AzoNO<sub>2</sub>** 87% (0.500 g, 1.21 mmol).

**AzoOCH<sub>3</sub>:** <sup>1</sup>H NMR (600 MHz, Chloroform-d, **Figure S5***a*) δ 7.96 – 7.86 (m, 4H), 7.69 (d, J = 8.6 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.41 (dd, J = 17.2, 1.4 Hz, 1H), 6.12 (dd, J = 17.3, 10.4 Hz, 1H), 5.86 (dd, J = 10.4, 1.3 Hz, 1H), 4.38 (t, J = 6.2 Hz, 2H), 4.08 (s, 3H), 3.72 (t, J = 6.2 Hz, 2H), 3.54 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).

HR-ESI-MS: calculated 398.1590, found 399.1663 (M + 1)

**AzoNO<sub>2</sub>:** <sup>1</sup>*H* NMR (600 MHz, Chloroform-d, **Figure S5b**)  $\delta$  8.39 (d, 1H), 8.15 (dd, J = 8.9, 2.4 Hz, 1H), 7.94 (d, J = 9.1 Hz, 2H), 7.77 (d, J = 8.9 Hz, 1H), 6.82 (d, J = 9.2 Hz, 2H), 6.42 (dd, J = 17.4, 1.3 Hz, 1H), 6.13 (dd, J = 17.3, 10.5 Hz, 1H), 5.87 (dd, J = 10.4, 1.3 Hz, 1H), 4.39 (t, J = 6.3 Hz, 2H), 3.74 (t, J = 6.3 Hz, 2H), 3.56 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H).

HR-ESI-MS: calculated 413.1335, found 436.1228 (M + Na<sup>+</sup>)



Figure S5. <sup>1</sup>H-NMR spectra of a) AzoOCH<sub>3</sub> and b) AzoNO<sub>2</sub> (600 MHz, Chloroform-d).



*Figure S6.* Normalized UV-Vis spectra of the four synthesized azo-dyes. The spectra were measured in ethanol, alone (0.1 wt.%) as well as together with the used photoinitiator BAPO with a concentration of 2 wt.%.

# DLP 3D Printing: Formulation and Printing Parameter Studies

The printing parameter screening was performed at the DLP utilizing its material test function. For this purpose, a droplet of the desired ink was placed on top of a 0.17 mm thin microscope slide, and a circular spot was projected with varying intensity and exposure times. After projection, uncured ink was rinsed, and the layer was carefully dried with compressed air. The cured film was measured using a calliper with a 0.01 mm precision.

Adapting the prior published formulation,<sup>5</sup> the SMP ink (10 g) was prepared by dissolving the particular azo-dye (0.1 wt.%, 10.0 mg) and BAPO (1.92 wt.%, 192.0 mg) in TCDMDA (18.5 wt.%, 1850 mg), PEGDA 575 (6.98 wt.%, 698.0 mg), IBA (70.6 wt.%, 7060 mg) and HA (1.90 wt.%, 190.0 mg). The formulation was left for 24h under vigorous stirring in a round bottom flask.

**Table S1.** Evaluation of the optimal concentration of the chlorine azo-dye compound in the liquid formulation. The LED irradiation time is the time required to complete the photopolymerization process under 380-390 nm UV light.

CI-Azo-dye Concentration	Irradiation time
(wt.%)	(s)
0.0	1.5
0.1	3.5
0.2	4.5
0.3	6.0
0.4	8.5
0.5	9.5
1.0	>15
2.0	>15

The optimal printing parameters for the formulations containing 0.1 w% of the respective azodye were investigated utilizing the material test function of the employed printer, as explained in the above. The irradiation intensity was set to 10 mW/cm<sup>2</sup> and the time was decreased subsequentially from 10 to 0.5 s. With the help of this procedure, the curing behaviour can be analysed directly from semilogarithmic plots of the experimentally obtained pairs of values being the depth of cure  $C_d$  (thickness of the cured layer) for each exposure energy E (product between intensity and time), as defined by Jacobs:<sup>6</sup>

$$C_d = D_p \ln\left(\frac{E}{E_c}\right),$$

(Equation S1)

Equation S1 allows to quantify the curing behaviour at the printer, i.e. the photonic parameters being the critical curing energy dose  $E_c$  (mJ/cm<sup>2</sup>) to cure a layer and the depth of light penetration  $D_p$  (cm) into the resin. The critical energy can be obtained from x-axis intercept of the semilogarithmic plots, so called "working curves", and the penetration depth from the slope

(Figure S7). Values for the critical energy were found in the range of 3.08 mJ/cm<sup>2</sup> (Cl) to 4.31 mJ/cm<sup>2</sup> (H). Penetration depths were in the region of 0.007 cm for all azo-dyes. For the blank formulation, i.e. the ink without azo-dye, the values for  $E_c$  and  $D_p$  differ slightly, being 2.81 mJ/cm<sup>2</sup> and 0.008 cm, respectively. The difference is due to the lower absorption of irradiation of the ink in the absence of the azo dye, resulting in lower curing energies and higher depths of penetration of the light into the ink. The employed working curve model is in good agreement with the data collected as indicated by R<sup>2</sup> (coefficient of determination) values above 0.98.



**Figure S7.** Working curves<sup>5</sup> for the inks including 2 wt % BAPO and 0.1 wt.% of the azo-dye compounds. A "blank" formulation (= no azo-dye) was studied as well for comparison.

Moreover, Jacobs working curves also allow to find optimal printing for different layer thicknesses (100  $\mu$ m, 50  $\mu$ m) reported in **Table S2**. The ideal exposure times for an irradiation intensity of 10 mW/cm<sup>2</sup> were found to be from 1.1 s (for blank formulation) to 2.0 s, allowing rapid 3D printing comparable to commercially available systems.

**Table S2.** Overview of the optimized 3D printing parameters as well as the obtained photonic parameters for the inks studied containing 2 wt % BAPO and 0.1 wt.% of azo-dye compound. A "blank" formulation (= no azo-dye) was studied as well for comparison.

Ink	Irradiation time (s)	Exposure Intensity (mW/cm²)	E <sub>c</sub> (mJ/cm²)	D <sub>p</sub> (mm)	R <sup>2</sup>
Blank	1.10		2.81	0.08	0.98
H-Azo-dye	2.00	10.00	4.31	0.07	0.98
Cl-Azo-dye	1.50		3.08	0.07	0.99
OCH <sub>3</sub> -Azo-dye	2.00		4.02	0.07	0.99
NO <sub>2</sub> -Azo-dye	1.75		4.13	0.08	0.99

### **FTIR-analysis**



*Figure S8.* FTIR spectra of the AzoCl-based ink and a printed structure before and after recovery.

The recorded FTIR-spectra for the ink and the printed structure ("as printed") have been used for estimating the double bond conversion (DOC).<sup>7</sup> In this particular case, the area of the signal of the double-bond band of the acrylate group at 809 cm<sup>-1</sup> was used in equation S2 and compared to the area of the stretching signal of the carbonyl groups at 1720 cm<sup>-1</sup>, since this band is not affected during printing:

 $DOC = 1 - \frac{A_{C=C}^{as \ printed} / A_{C=O}^{as \ printed}}{A_{C=O}^{ink}},$  (Equation S2)

For calculating the DOC, the regions of interest of the spectra were normalized and the baselines were corrected. Then, the peaks were fitted by Lorentz and Gaussian functions to obtain the area of each peak. Finally, the fitted peak areas were used to calculate the DOC using Equation S2. A DOC for about 85 % was estimated.



**Figure S9.** Section of the FTIR spectra of a) the AzoCl based ink and b) the corresponding 3D printed polymer used for the DOC calculation. Signals at 809 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> correspond to the double-bond band of the acrylate group and the band of the carbonyl group, respectively.

#### Analysis of the xy-resolution of the printed samples

After setting the optimal printing parameters, the achievable resolution of the systems containing azo-dyes was compared to the one of the blank ink (no azo-dye) to investigate the influence of the dyes in the printing performance. In 3D printing is important to distinguish between resolution along the Z-axis ("Z resolution") and resolution in the XY-plane ("XY resolution"). In DLP, Z resolution is given by the step motor of the printer and is usually reported in the spec sheets and known as minimum layer thickness. However, XY resolution depends on the microscopic imaging of the digital mirror device (DMD) of the DLP printer and the curing behaviour of the ink. The maximum, theoretically achievable XY resolution of an ink is thus the pixel size of the DMD in the printer, being 27 µm in our case (Asiga MAX X27 UV). Therefore, the XY resolution must be determined specifically each system and compared to the imaging unit of the printer. For this purpose, special tests specimens were designed.<sup>8</sup> The test structure consisted of a rectangular block with different engraved line gratings, whose line width and period ranged between 1000, 500, 250, 100, 50, 40, 30 µm. The models were printed as explained above and analysed using a high-resolution digital microscope. A detailed analysis of the resolution between the ideal model and the 3D prints is provided in Figure S9. The incorporation of the azo-dyes enhances the overall printing precision of the inks, reproducing the model more accurately.

a)





**Figure S9.** Analysis of the xy-resolution of the printed samples. Schematic representation of the test specimen geometry consisting of engraved line gratings with varying period and width is given in (a), where t is the thickness, h the depth and d the distance between the printed lines. Measured XY plane resolution of (b) blank formulation compared to (c - f) the formulations containing the azo-dyes.



Figure S11. DMA thermograms for all 3D printed samples. a) blank, b) H, c) Cl, d) OCH<sub>3</sub>, e) NO<sub>2</sub>.

Samala	First order Tg	First order Tg		
Sample	(°C)	(°C)		
Blank	81.1	31.9		
H-Azo-dye	76.4	25.9		
Cl-Azo-dye	80.0	30.2		
OCH₃-Azo-dye	77.3	31.1		
NO <sub>2</sub> -Azo-dye	80.6	26.2		

**Table S3.** Glass transition temperatures  $T_g$  for all the 3D printed samples calculated via DMA.



Figure S12. TGA thermograms for all 3D printed samples. a) Blank, b) H, c) Cl, d) OCH<sub>3</sub>, e) NO<sub>2</sub>.



**Figure S13.** DMA analyses under LED irradiation with an increasing current (A) of the LED power supply for 3D printed polymeric samples of a) blank formulation or containing compounds b) H, c) Cl, d) OCH<sub>3</sub>, e) NO<sub>2</sub>.



*Figure S14.* Calculation of the recovery parameter a for different 3D printed structures (rectangular stripe, frame, ring).



*Figure S15.* Shape-memory recovery of 3D printed (a) rectangular strips, (b) frames and (c) rings under LED irradiation for all azo-dye-based formulations.



**Figure S16.** Demonstration of the photothermal response of the fabricated 3D printed samples. Surface temperature of a 3D printed blank sample (without azo-dye) and a sample containing AzoCl before and after 10 s of laser irradiation. The measurement was performed at three different laser intensities: 1 %, 3 % and 5 % (approx. 99 mW, 344 mW and 567 mW).



*Figure S17.* Demonstration of the stability of the programmed shape over time at room temperature. Scale bar = 10 mm.

## REFERENCES

- 1. H. Jiang, G. Guo, W. Chen and Z. Cui, *Dyes and Pigments*, 2021, **194**, 109555.
- 2. E. Schab-Balcerzak, M. Siwy, M. Kawalec, A. Sobolewska, A. Chamera and A. Miniewicz, *The journal of physical chemistry. A*, 2009, **113**, 8765.
- 3. Q. Zhang, G. Vancoillie, M. A. Mees, R. Hoogenboom, *Polym. Chem.* 2015, **6**, 2396.
- 4. L. de Smet, G. Vancoillie, P. Minshall, K. Lava, I. Steyaert, E. Schoolaert, E. van de Walle, P. Dubruel, K. de Clerck and R. Hoogenboom, *Nat Commun*, 2018, **9**, 1123.
- 5. C. A. Spiegel, M. Hackner, V. P. Bothe, J. P. Spatz and E. Blasco, *Advanced Functional Materials*, 2022, 2110580.
- 6. P. Jacobs, *Rapid Prototyping & Manufacturing: Fundamentals of Stereolithography*, Society of Manufacturing Engineering, Dearborn, 1992.
- 7. A. S. Alketbi, Y. Shi, H. Li, A. Raza and T. Zhang, Soft Matter, 2021, 17, 7188-7195
- 8. What Does Resolution Mean in 3D Printing?, (last accessed August 2022).