## SUPPLEMENTARY INFORMATION

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Photomechanical Response in Physiological Conditions of Azobenzene-containing 4D Printed Liquid Crystal Elastomer Actuators

Lorena Ceamanos,<sup>a</sup> Dirk J. Mulder,<sup>b</sup> Zehra Kahveci,<sup>a</sup> María López-Valdeolivas,<sup>a</sup> Albert P.H.J. Schenning <sup>b,c</sup> and Carlos Sánchez-Somolinos \*<sup>a,d</sup>

<sup>&</sup>lt;sup>a</sup> Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, Zaragoza, 50009, Spain.

<sup>&</sup>lt;sup>b</sup> Laboratory of Stimuli-responsive Functional Materials and Devices (SFD), Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

<sup>&</sup>lt;sup>c.</sup> Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

<sup>&</sup>lt;sup>d.</sup> Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Nanomedicina, Instituto de Salud Carlos III, 50018 Zaragoza, Spain.
\*Correspondence: carlos.s@csic.es

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Figure S1. DSC of the oligomer precursor used for 4D printing of the LCEs.



Figure S2. Thermomechanical response in air of an uniaxially oriented LCE actuator (60  $\mu$ m thick) with the director along its long axis. Normalized length (L/L<sub>0</sub>) of the LC elastomer during the heating from 30 °C to 90 °C when is unloaded (grey squares) or coupled to a 1-gram weight (red circles).



Figure S3. Reversibility of the thermomechanical actuation of an uniaxially oriented LCE actuator (70  $\mu$ m thick) with the director along its long axis in air, PBS and FC-40. Normalized length (L/L<sub>0</sub>) of the LC elastomer at 30 °C before (initial state) and after heating (recovery). Normalized length before heating = 1.0.



Figure S4. Thermomechanical response in purified water (milliQ) of an uniaxially oriented LCE actuator (75  $\mu$ m thick) with the director along its long axis. Normalized length (L/L<sub>0</sub>) of the LC elastomer during the heating from 30 °C to 90 °C.



Figure S5. Reversibility of the photomechanical actuation of an uniaxially oriented LCE actuator (70  $\mu$ m thick) with the director along its long axis. Normalized length (L/L<sub>0</sub>) of the LC elastomer before UV irradiation (initial state), and after blue light irradiation (recovery). Normalized length before UV light irradiation = 1.0.



Figure S6. Experimental schemes for photomechanical experiments: Irradiation is applied by either a) one UV/blue LED stimulating one face of the sample or b) two UV/blue LEDs irradiating both sides of the sample. Equivalent total dose of photons between both setups is achieved by regulation of the intensity of exposure.



Figure S7. Photomechanical response in PBS at RT of a uniaxial oriented sample (70  $\mu$ m thick) with the director along its long axis. A weight of 1 g is attached to the lower extreme of the sample. (a) Normalized length (L/L<sub>0</sub>) of the LCE during UV irradiation using one LED (UV light at 180 mW/cm<sup>2</sup>, solid line) in comparison to the two LEDs (UV light at 90 mW/cm<sup>2</sup> each, dotted line) configuration. (b) Normalized contraction expressed in negative values (-C/C<sub>max</sub>) during exposure to UV light. Contraction is given in negative values to show the dynamic as a decay.



Figure S8. Photomechanical response in PBS at 37°C of a uniaxial oriented sample (70  $\mu$ m thick) with the director along its Iong axis. A weight of 1 g is attached to the lower extreme of the sample. (a) Normalized length (L/L<sub>0</sub>) of the LCE during UV<sub>L3</sub>, **00**, 1-3 | **5** irradiation using one LED (UV light at 180 mW/cm<sup>2</sup>, solid line) in comparison to the two LEDs (UV light at 90 mW/cm<sup>2</sup> each, dotted line) configuration. (b) Normalized contraction expressed in negative values (-C/C<sub>max</sub>) during exposure to UV light. Contraction is given in negative values to show the dynamic as a decay.



Figure S9. Thermomechanical response in air and FC-40 of uniaxial oriented LCEs ( $65\pm5 \ \mu m$  thick) with the director along its long axis. A load of 1 g attached to the extreme of the samples is lifted upon actuation. Normalized length (L/L<sub>0</sub>) of the LC elastomers during the heating from 30 °C to 90 °C. Mean±SD of two samples.



Figure S10. Photomechanical response in air at RT of a uniaxial oriented sample (70  $\mu$ m thick) with the director along its long axis when irradiating one face of the sample using one UV LED (180 mW/cm<sup>2</sup>, solid line) in comparison to two LEDs configuration (90 mW/cm<sup>2</sup> each, dotted line). A weight of 1 g is attached to the lower extreme of the sample. Society of Chemistry 20xx (a) Normalized length (L/L<sub>0</sub>) of the LC elastomer during UV irradiation. (b) Normalized contraction expressed in negative values (-C/C<sub>max</sub>) during exposure to UV light. Contraction is given in negative values to show the dynamic as a decay. (c) Temporal dependence of temperature of the LCE surface during UV light irradiation.