Supplementary Information

Bridging Sensing and Action: Autonomous Object Sorting by Reprogrammable Liquid Crystal Elastomers

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1. Experimental Section

Materials

Mesogenic diacrylates 1 4-(6-(Acryloyloxy)hexyloxy)phenyl 4-(6-(acryloyloxy)hexyloxy)benzoate (C6BAPE, ≥98%) and 1,4-Bis[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene (RM257, ≥97%) were purchased from Synthon Chemicals GmbH. Chain extender n-butylamine (≥99.5%) and solvent tetrahydrofuran (THF, ≥99.9%) were obtained from Merck. The UV photoinitiator 2-benzyl-2-(dimethylamino)−4'-morpholinobutyrophenone (Irgacure369, ≥97%) was acquired from Merck. The visible region absorbing dye N, N'-Bis(2,6-diisopropylphenyl)−3,4,9,10-perylenetetracarboxylic Diimide, also known as Perylene Orange (≥98%), was purchased from TCI Europe N.V. All molecules were used as received. The sacrificial support layer to release the LCE elements was made of polyvinyl alcohol (PVA; 80% hydrolyzed; Mw of 9000-10000) that was purchased from Aldrich.

LCE precursor ink preparation

The LCE precursor ink preparation followed the procedure developed and described by our group in previous work. [1,2] The process started by adding the two different mesogenic diacrylates, C6BAPE and RM257, to an amber flask, in a 1:1 molar ratio. In addition to them, the chain extender n-butylamine was incorporated into the flask in a 1:1.02 molar ratio. Besides, the photoinitiator (IRG369) was added in a 2 wt.% ratio, as well as the photoactive unit, Perylene Orange, in a 0.5 wt.%. The mixture was then solved into THF (1:1 weight ratio between mixture and solvent). The flask was closed and made it react for 30 min at 70 °C on a hot plate using a magnetic stirrer. After this short period, the flask was opened and left to react at the same temperature (70 °C) for 24 h additional hours to remove the solvent. After that, the flask was placed into a vacuum oven at 70 °C for 24 h more, to remove the residual fraction of the solvent and any bubble. As a final check, the weight of the photopolymerizable ink was compared to the mass of chemicals added initially, verifying that the residual level of THF was less than 1 wt.% (referred to as the weight of THF initially employed).

Printing equipment

The employed equipment for the printing process was a homebuilt 3D printer composed of a computer numerical control (CNC) router chassis coupled with a temperature-controlled reservoir for the ink. The ink was extruded through the needle by applying on-demand pressure while describing X, Y, and Z motions. Two software were used in the printing process, WinPC-NC for controlling the movements of the printer and AutoCAD for creating the computer-aided (CAD) files for the designed actuators. A 10 × 3 mm dog-bone-shaped actuator was created with the preferential orientation of the director, defined by the control of the printing direction, aligned with the long axis of the sample, for the thermal and photothermal characterization of the material. A 4-layer bimorph actuator with dimensions 12 × 3 mm (L x W), was fabricated. In the first two layers, the director orientation, determined by print

direction, aligns with the long axis of the sample. In the subsequent two layers, the orientation is orthogonal. Printing parameters, such as pressure, temperature, speed and distance between substrate and nozzle were optimized for each batch of photopolymerizable ink.

4D printing of LCE elements

The material was extruded from a light-protected syringe through a 23-gauge needle tip, with an inner diameter of 330 µm, and deposited on top of PVA-coated glasses. The printing process took place with the reservoir at 60 °C, while the substrate was kept at RT. For the PVA coating (150 nm) the glasses were first cleaned by ozone treatment and then a 5 wt.% PVA solution in Milli-Q purified water was spin-coated on top (1800 rpm for 60 s). Hereafter, the coating was fixed by drying the solution at 60 °C for 60 min. Single and multiple-layer actuators were manufactured, by raising the printhead a fixed height for each successive layer (typical height step of 60 µm). After printing each layer, the photopolymerization process took place under UV light.

Photopolymerization

After printing each layer, the actuator was exposed to the light from a UV lamp from Oriel (Model #6286) through a UV reflecting filter (350-450 nm, Model #66218), with a light intensity of 20 mW cm^{-2} for 2 min in ambient conditions. Subsequently, each side of the sample was irradiated for 12 min in a vacuum oven under a mild vacuum of 100 mbar at RT. This process was repeated with every single layer.

Photopolymerization yield

For quantifying the photopolymerization yield of the process, a gel fraction test was performed for every batch of ink prepared. For this purpose, an actuator is printed and photopolymerized following the procedure described above, and after that, its initial weight (w_i) is registered. Then, it is immersed in THF for 24 h, and after that, removed and dried for 4 h at 70 °C in a vacuum oven., and weighed again (w_f). The gel fraction is then assessed with Equation 1:

$$GF\ (\%) = \frac{w_f}{w_i} x\ 100 \qquad \textit{Equation 1}$$

Thermal characterization

DSC measurements were conducted in a TA Instruments DSC Q1000 system to determine the transition temperature of oligomers.

Polarization optical microscopy (POM)

To check the molecular alignment of the actuators, LCE were examined using a polarized optical microscope (Nikon Eclipse 80i).

Thickness Characterization

Thickness measurements of the actuators were performed using a profilometer (Bruker DektakXT Stylus Profiler).

Spectroscopic characterization

Absorption spectra of the samples were taken using a UV-Visible-NIR spectrophotometer (UV-Vis-NIR spectrophotometer Cary500, Agilent Technologies).

EPR characterization

An ELEXSYS E580e EPR spectrometer (Bruker), operating at X band (microwave frequency ca. 9.8 GHz) was used for taking the EPR spectra.

Actuation

Once extruded and photopolymerized, the samples, attached to the glass slide, were immersed in water to solve the PVA coating and release them. They were then let dry in ambient conditions for some hours by fixing a Kapton tape. The thermal actuation characterization of uniaxial actuators was made by using a home-built heated aluminum chamber with two windows of a cyclic olefin polymer (COP).[3] The transparency of the windows allowed us to take pictures with a digital camera Nikon D3300 for later measure the actuator's length and width. Moreover, one of the windows counts on a hole for an optimal registration of the surface temperature of the actuator with a thermal camera Gobi by Xenics. The actuator was placed inside the chamber with a 1 g load on its free end. The system was heated from RT to 100 °C with a rate of 5 °C min^{-1}, chosen based on the group's previous experience in this kind of experiment.[1,4] Pictures were taken every 5 °C, from which the length and width of the actuator were obtained by drawing a parallel line to the long axis of the strip and an orthogonal one, respectively, in Fiji. These values were then normalized by the values at RT for every sample and experiment.

On the other hand, photoactuation tests were performed under visible light, coming from a green LED (Thorlabs, central wavelength of 525 nm) or a far-red one (Thorlabs, central wavelength of 740 nm). Light intensities ranged from 50 to 200 mW cm^{-2}. For weight-lifting experiments, a similar method to the one employed in thermal actuation was used (uniaxial actuator with a 1 g load fixed to its free end). A video was recorded with a digital camera, and frames were later extracted to measure length and width as a function of time with Fiji as previously explained. Data on surface temperature were also registered with the thermal camera.

Sorting soft robot setup

A 4D printed bimorph LCE actuator was used for the purpose of demonstrating the sorting application. It was manufactured by addition of 4 layers, with dimensions of 12 x 3 mm (L x W). The first two layers were printed aligning the director with the long axis of the rectangle, whereas the two layers on top had the director aligned with the short axis.

A light setup composed of the two LEDs previously mentioned was used for the assembly of the sorting soft robot. The green LED was placed on top, while the far-red LED irradiated from below. The sample was placed between these two light sources. A dark mask was placed between the sample and the green light source, allowing only the free-tip half of the sample to be irradiated. To reproduce the roller conveyor in an easy and small way, small plastic parts were printed with the help of an Anycubic PhotonS Stereolithography Printer on a commercial resin. To hold the elements to be sorted, two needles were used. The translocated COP sheets were 17 x 5 mm, with a thickness of 50 µm. To obtain the red-colored COP sheets, 5 minutes of ozone surface treatment was applied, and subsequently, they were dyed by coloring them with a conventional red permanent marker pen.

2. Supplementary Figures

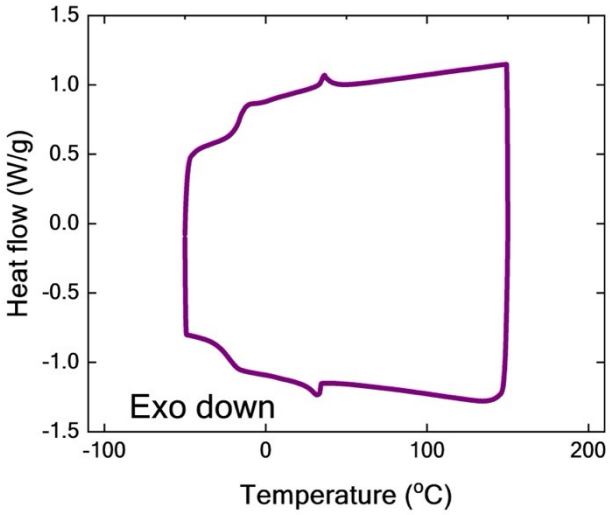

Fig. S1 DSC of the oligomer precursor used for 4D printing of the LCEs.

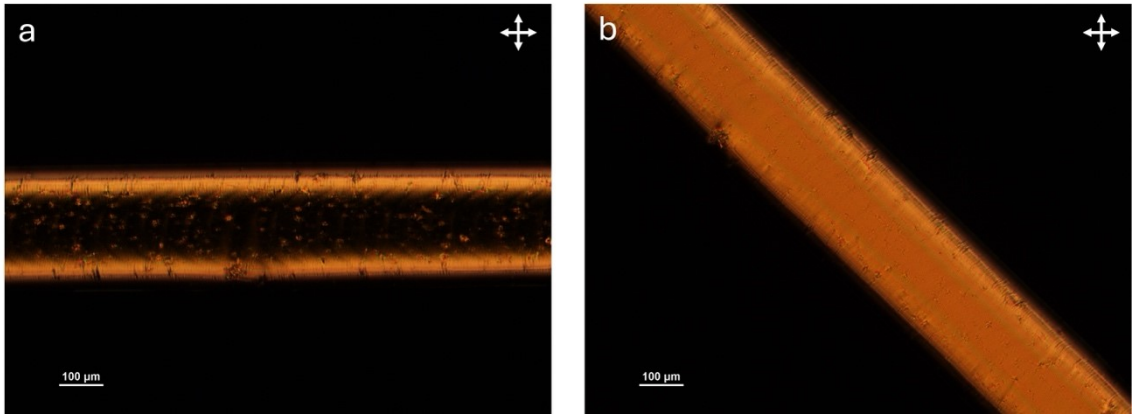

Fig. S2 POM images of LCE printed lines acquired before photopolymerization between crossed polarizers (crosses indicate polarizer transmission directions) with the printing direction oriented (a) parallel and (b) at 45° with respect to the first polarizer transmission direction. Scale bar represents 100 µm.

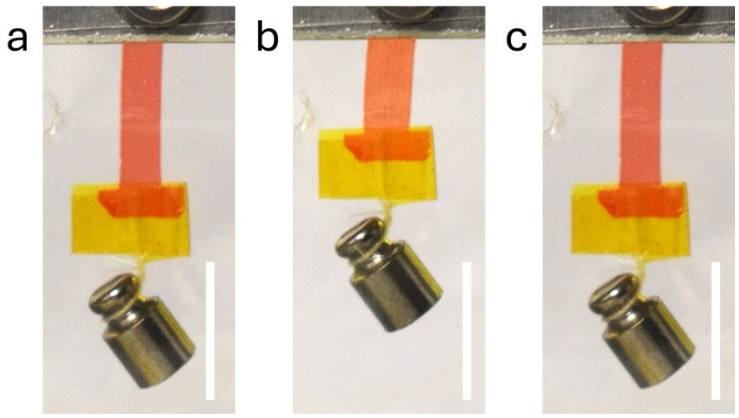

Fig. S3 Thermoactuation test on a sample loaded with 1 g weight, at 27 °C (a), 100 °C (b) and after cooling down back to RT (c). Scale bar represents 10 mm.

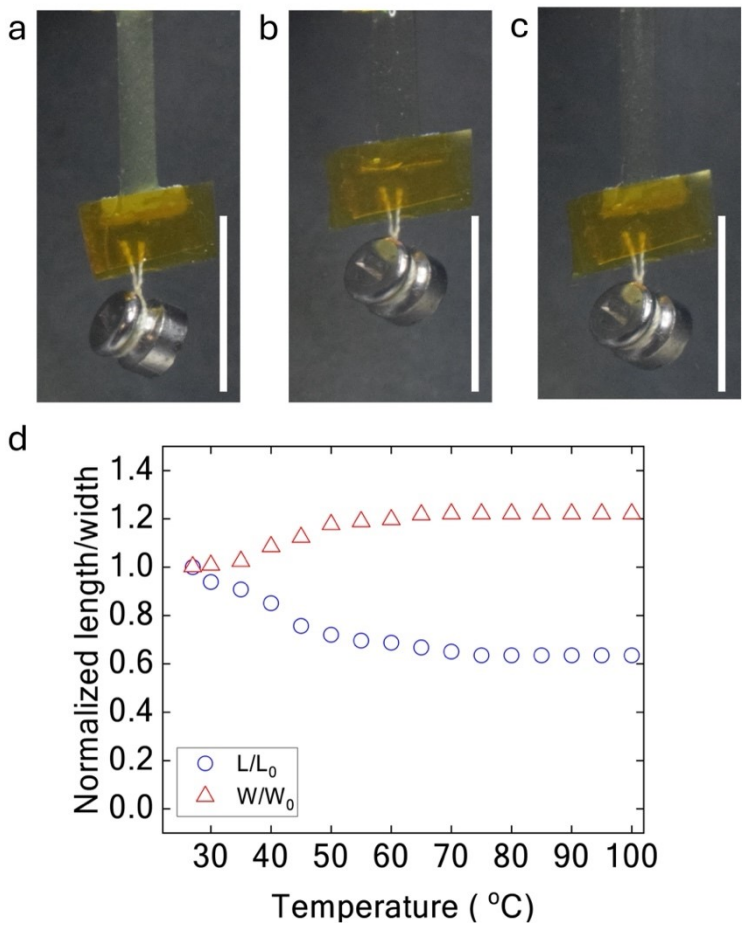

Fig. S4 Thermoactuation test on an uniaxially oriented LCE strip (100 µm thick) with the director along its long axis and a 1 g weight attached to its free end. The actuator does not contain PO in its formulation. Pictures taken at 27 °C (a), 100 °C (b) and after cooling down back to RT (c). Scale bar represents 10 mm. (d) Temperature dependence of the normalized length and width of both LCE strips during the heating process.

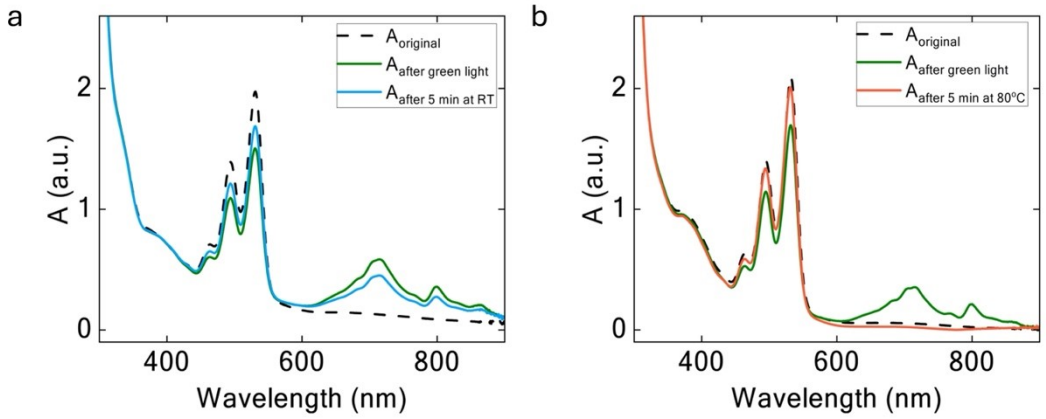

Fig. S5 (a) Absorption spectra of a 100 μm thick LCE actuator measured before green irradiation (dashed black lines), immediately after irradiation with green light (100 mW cm^{-2}, 30 s) (solid green line), and 5 minutes after irradiation while maintained at RT (solid blue line). (b) Same measurements as in (a), but the actuator was maintained at 80 °C during the 5-minute post-irradiation period. The spectrum measured after this period is shown as a solid red line.

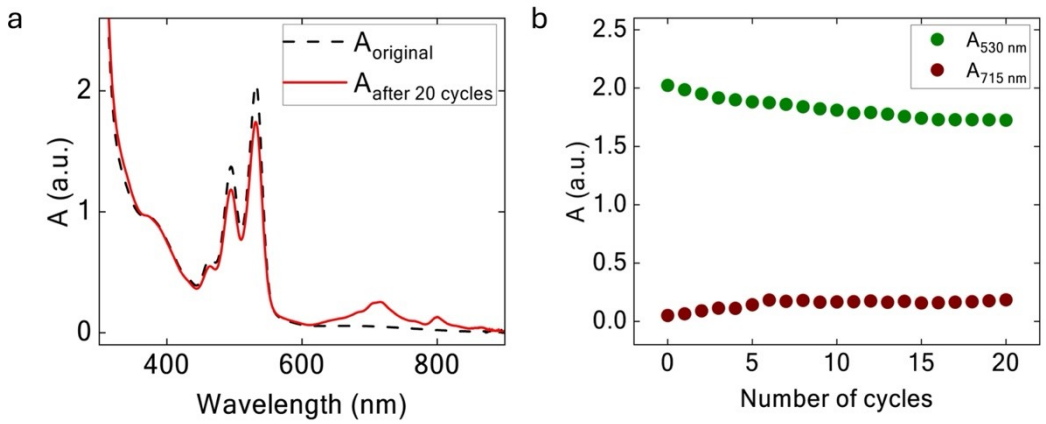

Fig. S6 Absorption spectra of a 100 μm thick actuator subjected to 20 cycles of light irradiation. Each cycle consisted of 30 s of green light (525 nm, 100 mW cm^{-2}), followed by 2 min of far-red light irradiation (740 nm, 450 mW cm^{-2}). (a) The dashed black line corresponds to the initial spectrum, while the solid red line shows the spectrum after 20 cycles. (b) Evolution of the absorption at the main peaks in the green and far-red regions (530 and 715 nm, respectively) measured after each cycle over 20 cycles.

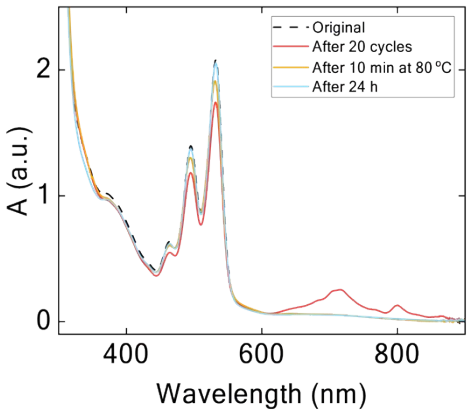

Fig. S7 Absorption spectra of a 100 μm thick LCE actuator. The dashed black line corresponds to the initial spectrum, while the solid red line represents the spectrum after 20 cycles of light irradiation (similar as in Fig. S6a). Each cycle consisted of 30 s of green light (525 nm, 100 mW cm^{-2}) followed by 2 min of far-red light (740 nm, 450 mW cm^{-2}) for 2 minutes. The LCE actuator was then heated up to 80 °C for 10 minutes, and the absorption spectrum again registered (solid orange line). After 24 hours at ambient conditions, the absorption was re-registered (solid blue line).

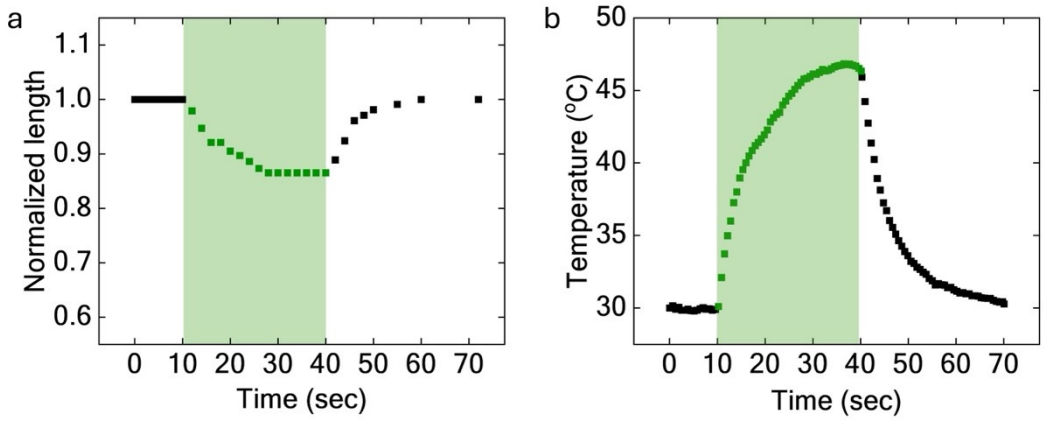

Fig. S8 Evolution over time of the normalized length (a) and the temperature (b) of a uniaxial LCE actuator during green light irradiation (100 mW cm^{-2}, 30 s). The green light exposure period is indicated by a green band in the plot. The green squares represent the contraction along the long axis and the increment of temperature during green light exposure. The black squares correspond to the recovery of the initial values after green light is switched off.

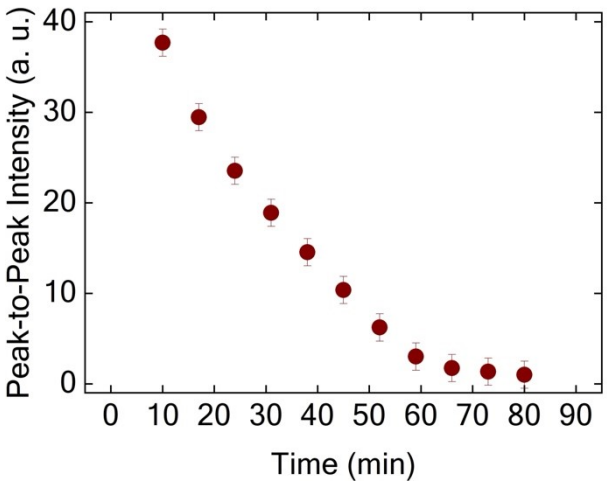

Fig. S9 Time evolution of the EPR peak-to-peak signal intensity after the actuator was exposed to green light of 100 mW cm^{-2} for 30 seconds. Typical time evolution of the EPR signal intensity is fully compatible with that of the 715 nm absorption peak after green light irradiation (Fig. 3b).

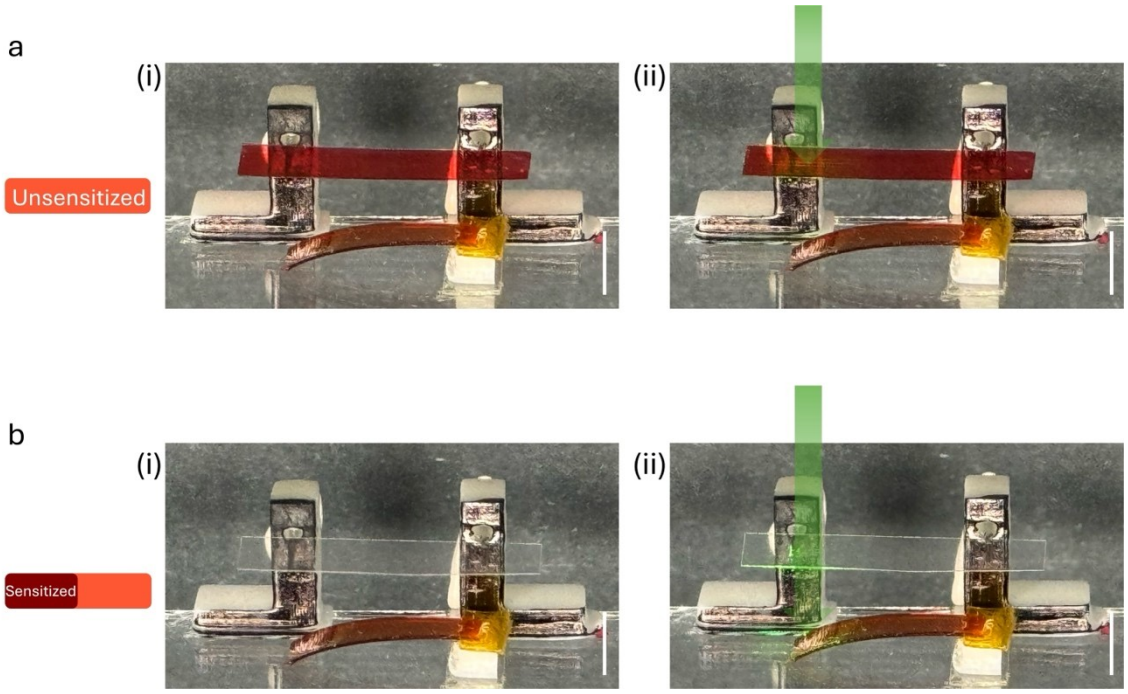

Fig. S10 Description of the transmission of green light in the soft sorting robotic system. (a) The unsensitized system includes a red-colored sheet (i) that, when green light coming from the top, absorbs it (ii). (b) On the other hand, the sensitized actuator includes a transparent sheet (i) that does not block the passage of green-light (ii), reaching the actuator and sensitizing it to far-red light. Green arrows indicate green light coming from the top. Scale bar represents 5 mm.

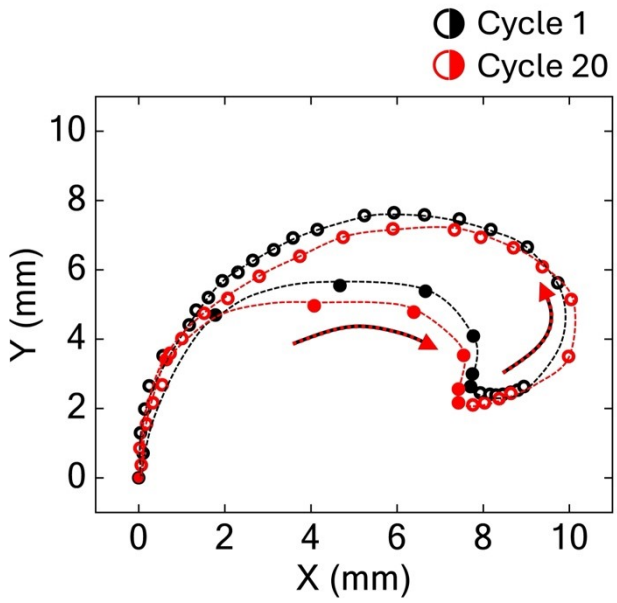

Fig. S11 Comparison of the tip trajectories of a far-red sensitized 4D printed bimorph LCE actuator under far-red light irradiation over cycles. The XY coordinates of the actuator tip are plotted for both the first cycle (black) and the twentieth cycle (red) states. Solid circles represent the bending trajectory, while hollow circles indicate the unbending phase. After each non-reciprocal motion, a sufficient dose of far-red illumination was applied to promote depletion of the radical species generated (400 mW cm^{-2}, 10 min). Note that lines are drawn to guide the eye.

3. Supplementary Movies

Movie S1. Photoactuation of a 4D printed bimorph LCE actuator doped with Perylene Orange, in its unsensitized state under far-red light (740 nm). Demonstration of the behavior of a 4D printed bimorph LCE actuator in its unsensitized state under far-red light. To this purpose, the strategy is performed on a 4-layer bimorph LCE actuator doped with 0.5 wt% of Perylene Orange. The irradiation scheme is based on a far-red light (740 nm) irradiation of 400 mW cm^{-2} for 12 seconds. The video is played at 10x speed for a better visualization of the movement.

Movie S2. Photoactuation of a 4D printed bimorph LCE actuator doped with Perylene Orange, in its sensitized state under far-red light (740 nm). Demonstration of the behavior of a 4D printed bimorph LCE actuator in its sensitized state under far-red light. To this purpose, the strategy is performed on a 4-layer bimorph LCE actuator doped with 0.5 wt% of Perylene Orange. The irradiation scheme is based on an irradiation with green light (525 nm) of 100 mW cm^{-2} for 30 seconds. Once the green light is switched off, the LCE element is led to cool down and once recovered RT, a far-red light (740 nm) irradiation of 400 mW cm^{-2} takes place for 12 seconds. The video is played at 10x speed for a better visualization of the movement.

Movie S3. Sorting of a red-colored sheet by a 4D printed bimorph LCE actuator doped with Perylene Orange. Demonstration of the approach of a sorting soft robot based on a reprogrammable photosensitive 4D printed bimorph LCE actuator sorting a red-colored COP sheet to the right. The irradiation scheme is based on a first step of irradiation with green light (525 nm) of 100 mW cm^{-2} for 30 seconds. This light, coming from the top and covering the free-tip half of the LCE actuator, is absorbed by the red-colored COP sheet as indicated with a green arrow. Once the green light is switched off, the LCE element is led to cool down and once recovered RT, a far-red light (740 nm) irradiation of 400 mW cm^{-2} takes place for 12 seconds. The video is played at 10x speed for better visualization of the sorting process.

Movie S4. Sorting of a transparent sheet by a 4D printed bimorph LCE actuator doped with Perylene Orange. Demonstration of the approach of a sorting soft robot based on a reprogrammable photosensitive 4D printed bimorph LCE actuator sorting a transparent COP sheet to the left. The irradiation scheme is based on a first step of irradiation with green light (525 nm) of 100 mW cm^{-2} for 30 seconds. This light, coming from the top and covering the free-tip half of the LCE actuator, is not absorbed by the transparent-colored COP sheet and reaches the LCE actuator, which absorbs the light, as indicated with a green arrow. Once the green light is switched off, the LCE element is led to cool down and once recovered RT, a far-red light (740

nm) irradiation of 400 mW cm^{-2} takes place for 12 seconds. The video is played at 10x speed for better visualization of the sorting process.

4. References

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4 L. Ceamanos, Z. Kahveci, M. López-Valdeolivas, D. Liu, D. J. Broer and C. Sánchez-Somolinos, *ACS Appl. Mater. Interfaces*, 2020, **12**, 44195–44204.