Making waves in a photoactive polymer film

Anne Helene Gelebart1,2, Dirk Jan Mulder1, Michael Varga3, Andrew Konya3, Ghislaine Vantomme2, E. W. Meijer2, Robin L. B. Selinger3 & Dirk J. Broer1,2

Oscillating materials1–4 that adapt their shapes in response to external stimuli are of interest for emerging applications in medicine and robotics. For example, liquid-crystal networks can be programmed to undergo stimulus-induced deformations in various geometries, including in response to light5,6. Azobenzene molecules are often incorporated into liquid-crystal polymer films to make them photoresponsive7–11; however, in most cases only the bending responses of these films have been studied, and relaxation after photo-isomerization is rather slow. Modifying the core or adding substituents to the azobenzene moiety can lead to marked changes in photophysical and photochemical properties12–15, providing an opportunity to circumvent the use of a complex set-up that involves multiple light sources, lenses or mirrors. Here, by incorporating azobenzene derivatives with fast cis-to-trans thermal relaxation into liquid-crystal networks, we generate photoactive polymer films that exhibit continuous, directional, macroscopic mechanical waves under constant light illumination, with a feedback loop that is driven by self-shadowing. We explain the mechanism of wave generation using a theoretical model and numerical simulations, which show good qualitative agreement with our experiments. We also demonstrate the potential application of our photoactive films in light-driven locomotion and self-cleaning surfaces, and anticipate further applications in fields such as photomechanical energy harvesting and miniaturized transport.

We followed two well-known strategies for reducing the thermal relaxation time of an azobenzene: (i) adding a push–pull group and (ii) forming a tautomerizable azohydrazone16. Correspondingly, we designed two polymerizableazo-derivatives (Fig. 1, Extended Data Fig. 1). The first molecule corresponds to a hydrogen-bonded azopyridine (I) and the second one has a hydroxyl group at the ortho position (II). Each azo-derivative (7 mol%) was copolymerized with a mixture of a liquid-crystal monoa crylate (RM23, 42 mol%) and a liquid-crystal diacrylate (RM82, 50 mol%), initiated by 1 mol% of photoinitiator. The mixtures containing I and II are henceforth denoted as mixtures I and II, respectively, and the azo-derivatives themselves are referred to simply as I or II. The monomer mixture was aligned before polymerization in a splayed configuration over the cross-section of a thin film, with homeotropic alignment at one surface and planar alignment at the other. This splay-aligned configuration was chosen because it gives rise to the largest deformation in free-standing films, as compared to uniaxial alignment, owing to the expansion and shrinkage behaviour that occurs on opposite sides of the liquid-crystal network (LCN) film, as explored in ref. 17 and shown in Supplementary Video 1.

We studied the thermal relaxation of LCN films made of mixtures I and II using ultraviolet spectroscopy, and compared them to LCNs containing: (i) A6MA, a commonly used azobenzene for photoresponsive materials; (ii) Disperse Red 1 acrylate (DR1A), a known commercial ultrafast azo-derivative; and (iii) AzoPy, which corresponds to I without the hydrogen bond. See Extended Data Fig. 2 and Extended Data Table 1 for the compositions of the mixtures and their thermal characterization.

As shown in Fig. 1, at room temperature, the half-life of A6MA is long, typically more than 1 h, whereas azo-derivatives I and II exhibit much faster relaxation. However, temperature plays an important part in the relaxation process (Fig. 1 and Extended Data Fig. 3), and the half-life drops below 1 s at 70 °C and 90 °C for II and I, respectively.

Figure 1 | Azo dyes and their cis-to-trans relaxation. a, Chemical structures of azo-derivatives and liquid crystal mesogens. b, The half-lives of the cis-to-trans relaxation of the azo-derivatives decrease exponentially as a function of temperature.
Comparing AzoPy with I shows that the hydrogen bond enhances the push–pull effect, which results in a further decrease in the half-life. As predicted, the thermal relaxation of DR1A is very fast, less than 1 s at 30 °C. Furthermore, the cis-to-trans thermal relaxation of the azo-derivatives follows a stretched exponential function, as previously described for such glassy materials

With the aim of translating this fast molecular relaxation to the macroscopic deformation of the LCNs, small thin strips of the polymer were clamped at one end and exposed to ultraviolet light. As previously reported, when A6MA is used, the film bends and remains in this position when the light is switched off. When I or II is used, the bending and relaxation are both instantaneous as illumination is applied and removed. However, on the basis of the molecular relaxation at room temperature, the time to full recovery is expected to be more than 10 min and about 1 min for I and II, respectively, which is much slower than the observed macroscopic deformation. This faster recovery can be explained by a large increase in the temperature of the film of several tens of degrees during ultraviolet exposure. In the exposed films, we recorded temperatures of up to 85 °C—higher than the glass transition temperature ($T_g$) of the LCN, which is measured to be around 50 °C. At this temperature, the half-life decreases to 2 s and less than 1 s for I and II, respectively. It has recently been shown that in the direct vicinity of the azobenzene molecules the temperature can reach 228 °C, and even higher temperatures have been calculated. On the basis of these findings, we postulate that the molecular relaxation of the azobenzene moieties is faster because of the higher temperatures; hence, we expect even faster macroscopic relaxation.

To benefit from this fast relaxation, we studied different sample configurations. When a strip of a thin LCN film made of mixture I is placed on a glass surface, enabling free movement without further constraints, the polymeric film deforms in a caterpillar-like fashion. When the film is clamped at one end only, we observe oscillations similar to those reported in ref. 6. Finally, when two edges of the film are glued together, a tube forms. On illumination, the tube buckles and continuously deforms, as shown (in real time) in Supplementary Video 2.

More interestingly, when the same film (that is, made from mixture I) is attached at both ends to a substrate and exposed to light (405 nm), a continuous travelling wave is initiated. Because the distance between the two ends is shorter than the length of the strip, a buckled initial shape is created (Fig. 2a). Turning on a fixed light source initiates a wave
that continuously regenerates and propagates in a repeating, snake-like motion until the light is turned off. Similar results were obtained when using a film made of mixture II or DR1A, which has an extremely short half-life of 1.9 s at 25 °C. However, when using an LCN containing A6MA, no continuous wave could be obtained owing to the thermal relaxation being too slow (see Supplementary Video 3). This result suggests that the wave propagation is not restricted to the custom-made azo-derivatives; we anticipate that any molecule with a short half-life could give rise to such types of deformation. In the rest of this study, LCN films made with mixture I were used.

The use of a splay-aligned LCN gives an extra degree of control to the system: the direction of the wave is controlled by the orientation of the film with regard to the planar and homeotropic sides. As demonstrated in Fig. 2a, when the planar side is placed upwards, the induced wave propagates away from the light source; when the homeotropic side is up, the wave propagates towards the light source. Supplementary Videos 4 and 5 show (in real time) this light-induced periodic wave motion for planar-up and homeotropic-up configurations, respectively.

These two distinct wave trajectories are driven by the different phototactic responses of the two sides of the film. On illumination, the planar side shrinks strongly along the long axis of the film and expands weakly along the other two axes, causing the light-exposed area to curve downwards. In contrast, the homeotropic side shrinks strongly along the thickness axis of the film and expands weakly along the other two axes, causing the light-exposed area to curve upwards. Both types of deformation also induce slight curvature across the short axis of the film, as in a ‘slap band’ bracelet. This slight deformation can produce mechanical instabilities such as snap-through transitions. As discussed further below, effects from self-shadowing produce a feedback loop that enables wave propagation and regeneration, because continuous displacement of the wave changes the position of the exposed and unexposed areas.

The speed of the displacement is greatly influenced by whether the planar or the homeotropic side is facing the light source. With the planar side towards the oblique incoming light, the wave travels in the direction away from the lamp with a frequency of 2.5 s⁻¹. When the film is flipped to put the homeotropic side upwards, the wave has a slower frequency of 0.8 s⁻¹ under the same exposure conditions, and the wave travels towards the light.

The incident angle between the light and the film is also found to influence the propagation speed of the generated waves. The wave propagates for angles of 0°–45° with the planar side up and of 0°–15° with the homeotropic side up (Fig. 2b and Extended Data Fig. 4). Above these critical values, the film becomes fully exposed, cancelling the self-shadowing effect. This working range of angles is valid for distances between the two attached points of 2.2–1.6 cm for a film with an initial length of 2.3 cm, for example, buckled with the end-to-end distance reduced by up to 30%. In the planar-up configuration, a maximum speed is found for angles of 10°–25°. The intensity of the light also greatly influences the speed at which the waves travel. As shown in Fig. 2c, for a sample illuminated at an intensity of 510 mW cm⁻², a frequency of 3 s⁻¹ is reached. When the intensity is reduced to 230 mW cm⁻², the frequency decreases to 0.5 s⁻¹. The motion stops entirely for light intensities of less than 175 mW cm⁻², owing to the photo-thermal effect. For intensities below 150 mW cm⁻², the temperature remains below the glass transition temperature Tg (Extended Data Fig. 5a). A reference measurement with a uniaxially aligned film did not result in wave deformation, despite crossing Tg on illumination (Extended Data Fig. 5b).

As mentioned above, temperature plays an important part, as shown in Fig. 3. On exposure, the overall temperature of the film rises to roughly 50 °C. When the wave reaches the clamped end of the film, it arrests for a short period before a new wave forms and starts to propagate. During this very short period, the temperature reaches values close to 100 °C (Fig. 3 and Extended Data Fig. 6; Supplementary Videos 4 and 5). The substantial heat generated also contributes to the deformation through thermal expansion, and is considered in the mechanism of creation and propagation of the wave.

To gain insight into the mechanism of this wave generation and its directionalit,y, we carried out finite-element elastodynamics analysis. We consider an LCN film with a ‘blueprinted’ director field, with the director homeotropic on one side and planar on the other with a linear gradient in between producing splay alignment (Fig. 2a).

In simulations, the film is initially buckled into a curved shape, clamped at both ends on a solid substrate, then relaxed to mechanical equilibrium. We model incoming light as a plane wave from the left side of the sample at an angle of 10° above the horizontal. To determine which elements on the film surface are illuminated, incident light is represented as a grid of parallel rays and their first intersection with the surface is calculated. We model the light-induced motion of the film using a Hamiltonian-based elastodynamics algorithm with explicit time stepping. Our Hamiltonian-based model includes the kinetic energy of the film, its elastic strain energy and the coupling between nematic order and mechanical strain. Details of the simulation model are provided in Methods.

To model photoactuation, we make a rough approximation that the scalar order parameter S in each element along the surface decreases linearly in time when illuminated and increases linearly in time when shadowed, bounded by upper and lower limits. As S decreases within a volume element, coupling between nematic order and strain causes the material to shrink along the local director and expand in the two orthogonal directions. The decrease in S can be caused by either the isomerization of the azo units or the thermal expansion that is induced by the light exposure. In Fig. 2d, e, the colour indicates the magnitude of the scalar order parameter S, with blue and red regions showing the lowest and highest values, respectively.

The results of our simulations demonstrate the feedback mechanism that continuously generates waves. Consider first the planar-up configuration (Fig. 3a and b). During the initial stage of illumination (Fig. 3a), the colour indicates the magnitude of the scalar order parameter S, with blue and red regions showing the lowest and highest values, respectively.

In the planar-up configuration, a maximum speed is reached for angles of 10°–25°. The intensity of the light also greatly influences the speed at which the waves travel. As shown in Fig. 2c, for a sample illuminated at an intensity of 510 mW cm⁻², a frequency of 3 s⁻¹ is reached. When the intensity is reduced to 230 mW cm⁻², the frequency decreases to 0.5 s⁻¹. The motion stops entirely for light intensities of less than 175 mW cm⁻², owing to the photo-thermal effect. For intensities below 150 mW cm⁻², the temperature remains below the glass transition temperature Tg (Extended Data Fig. 5a). A reference measurement with a uniaxially aligned film did not result in wave deformation, despite crossing Tg on illumination (Extended Data Fig. 5b).

As mentioned above, temperature plays an important part, as shown in Fig. 3. On exposure, the overall temperature of the film rises to roughly 50 °C. When the wave reaches the clamped end of the film, it arrests for a short period before a new wave forms and starts to propagate. During this very short period, the temperature reaches values close to 100 °C (Fig. 3 and Extended Data Fig. 6; Supplementary Videos 4 and 5). The substantial heat generated also contributes to the deformation through thermal expansion, and is considered in the mechanism of creation and propagation of the wave.

To gain insight into the mechanism of this wave generation and its directionality, we carried out finite-element elastodynamics analysis. We consider an LCN film with a ‘blueprinted’ director field, with the director homeotropic on one side and planar on the other with a linear gradient in between producing splay alignment (Fig. 2a).

In simulations, the film is initially buckled into a curved shape, clamped at both ends on a solid substrate, then relaxed to mechanical equilibrium. We model incoming light as a plane wave from the left side of the sample at an angle of 10° above the horizontal. To determine which elements on the film surface are illuminated, incident light is represented as a grid of parallel rays and their first intersection with the surface is calculated. We model the light-induced motion of the film using a Hamiltonian-based elastodynamics algorithm with explicit time stepping. Our Hamiltonian-based model includes the kinetic energy of the film, its elastic strain energy and the coupling between nematic order and mechanical strain. Details of the simulation model are provided in Methods.

To model photoactuation, we make a rough approximation that the scalar order parameter S in each element along the surface decreases linearly in time when illuminated and increases linearly in time when shadowed, bounded by upper and lower limits. As S decreases within a volume element, coupling between nematic order and strain causes the material to shrink along the local director and expand in the two orthogonal directions. The decrease in S can be caused by either the isomerization of the azo units or the thermal expansion that is induced by the light exposure. In Fig. 2d, e, the colour indicates the magnitude of the scalar order parameter S, with blue and red regions showing the lowest and highest values, respectively.
There is qualitative agreement between the simulated trajectories and experimental observations (see Supplementary Videos 4 and 5). The simulations demonstrate that light-induced actuation, self-shadowing and mechanical constraints are sufficient to create a feedback loop, producing wave generation that is driven by a constant light source. Additional simulations show that both pre-buckling the film and clamping it on a solid substrate are necessary to enable the pop-through transition at the end of each cycle.

To demonstrate the versatility of our experimental system, we developed a few examples where wave propagation is used to achieve light-driven devices. First, we place sand on the film, either before or during illumination, at the side of the origin of the wave (Fig. 4a). While the wave develops, the sand is continuously transported towards the opposite side of the film. When energy is stored in the film, for instance when the weight of the sand inhibits wave propagation, the film suddenly releases the energy, ejecting the sand far from the film. The film can be used many times without showing any damage or fatigue with respect to the sand or the light. Second, we used the LCN film to carry uphill an object that is much heavier and larger in size than itself. The repeated propagation of the wave makes such a challenging operation possible by simultaneously pushing the object upwards and preventing it from sliding (Supplementary Video 6). Finally, and most remarkably, we realized a light-fuelled self-propelled device using photoactuated mechanical wave generation. When the LCN is attached to a plastic frame (Fig. 4b), the device moves while the wave is travelling through the sample. The travelling direction is controlled by the orientation of the film, as described previously, demonstrating directional light-induced locomotion. Small objects (with masses of a few milligrams) can be attached to the frame and transported over large distances (centimetres). Videos (in real time) of the light-fuelled device are provided in Supplementary Videos 7 and 8. We anticipate that the generation of waves as demonstrated here has potential applications in fields such as photomechanical energy harvesting, self-cleaning by contaminant rejection, and miniaturized transport of species in poorly accessible places.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Received 19 January; accepted 16 May 2017.

1. Tabata, O., Hirasa, H., Aoki, S., Yoshida, R. & Kokufuta, E. Ciliary motion actuator using self-oscillating gel. Sensor. Actuat. A 95, 234–238 (2000).
2. Murase, Y., Maeda, S., Hashimoto, S. & Yoshida, R. Design of a mass transport surface utilizing peristaltic motion of a self-oscillating gel. Langmuir 25, 483–489 (2009).
3. Maeda, S., Hara, Y., Yoshida, R. & Hashimoto, S. Peristaltic motion of polymer gels. Angew. Chem. Int. Ed. 47, 6690–6693 (2008).
4. Maeda, S., Hara, Y., Sakai, T., Yoshida, R. & Hashimoto, S. Self-walking gel. Adv. Mater. 19, 3480–3484 (2007).
5. Martinez, A. & Smalyukh, I. I. Light-driven dynamic Archimedes spirals and periodic oscillatory patterns of topological solitons in anisotropic soft matter. Opt. Express 23, 4591–4604 (2015).
6. White, T. J. et al. A high frequency photodriven polymer oscillator. Soft Matter 4, 1796–1798 (2008).
7. Yu, Y., Nakano, M. & Ikedu, T. Photomechanics: directed bending of a polymer film by light. Nature 425, 145 (2003).
8. van Oosten, C. L., Harris, K. D., Bastiaansen, C. W. M. & Broer, D. J. Glassy photomechanical liquid-crystal network actuators for microscale devices. Eur. Phys. J. E 23, 329–336 (2007).
9. Li, M.-H., Keller, P., Li, B., Wang, X. & Bruin, M. Light-driven side-on nematic elastomer actuators. Adv. Mater. 15, 569–572 (2003).
10. Ilmuard, S. et al. Conversion of light into macroscopic helical motion. Nat. Chem. 6, 229–233 (2014).
11. Yamada, M. et al. Photomobile polymer materials: towards light-driven plastic motors. Angew. Chem. Int. Ed. 47, 4986–4988 (2008).
12. Bandara, H. M. D. & Burdette, S. C. Photoisomerization in different classes of azobenzene. Chem. Soc. Rev. 41, 1899–1925 (2012).
13. García-Amorós, J. & Velasco, D. Recent advances towards azobenzene-based light-driven real-time information-transmitting materials. Beilstein J. Org. Chem. 8, 1003–1017 (2012).
14. van Oosten, C. L., Bastiaansen, C. W. M. & Broer, D. J. Printed artificial cilia from liquid-crystal network actuators modularly driven by light. Nat. Mater. 8, 677–682 (2009).
15. Camacho-Lopez, M., Finkelmann, H., Palffy-Muhoray, P. & Shelley, M. Fast liquid-crystal elastomer swims into the dark. Nat. Mater. 3, 307–310 (2004).
16. Brode, W. R., Gould, J. H. & Wyman, G. M. The relation between the absorption spectra and the chemical constitution of dyes. XXV. Phototropism and cis-trans isomerism in aromatic azo compounds. J. Am. Chem. Soc. 74, 4641–4646 (1952).
17. Mol, G. N., Harris, K. D., Bastiaansen, C. W. M. & Broer, D. J. Thermo-mechanical responses of liquid-crystal networks with a splayed molecular organization. Adv. Funct. Mater. 15, 1155–1159 (2005).
18. Mita, I., Horie, K. & Hiroa, K. Photochemistry in polymer solids. 9. Photoisomerization of azobenzene in a polycarbonate film. Macromolecules 22, 558–563 (1989).
19. Poutanen, M., Ikkala, O. & Priimagi, A. Structurally controlled dynamics in azobenzene-based supramolecular self-assemblies in solid state. Macromolecules 49, 4099–4101 (2016).
20. Serra, F. & Terentjev, E. M. Effects of solvent viscosity and polarity on the isomerization of azobenzene. Macromolecules 41, 981–986 (2008).
21. Vapaavuori, J., Laventure, A., Bazuin, C. G., Lebel, O. & Pellerin, C. Submolecular plasticization induced by photons in azobenzene materials. J. Am. Chem. Soc. 137, 13510–13517 (2015).
22. Fang, G. J. et al. Athermal photofluidization of glasses. Nat. Commun. 4, 1521 (2013).
23. Sawa, Y. et al. Shape and chirality transitions in off-axis twist nematic elastomer ribbons. Phys. Rev. E 88, 022502 (2013).
24. Konya, A., Gimenez-Pinto, V. & Selinger, R. L. B. Modeling defects, shape evolution, and programmed auto-origami in liquid crystal elastomers. Front. Mater. 3, 24 (2016).
25. de Haan, L. T. et al. Accordion-like actuators of multiple 3D patterned liquid crystal polymer films. Adv. Funct. Mater. 24, 1251–1258 (2014).

Supplementary Information is available in the online version of the paper.

Acknowledgements This work was supported financially by the Netherlands Organization for Scientific Research (NWO; TOP PUNT grant 10018944), the European Research Council (Vibrate ERC, grant 669991), and US National Science Foundation grants DMR 1409658 and CMMI 1436565. A.H.G. acknowledges funding from the People Programme (Marie Curie Actions) of the European Union’s Seventh Framework Programme FP7-2013, grant number 607602. Computing resources provided by the Ohio Supercomputer Center (M.V., A.K., R.L.B.S.) R.L.B.S. acknowledges F. Nazarov for discussions and B. L. Mbanga for his role in developing the Finite Element Method algorithm. The work of D.J.M. forms part of the research programme of the Dutch Polymer Institute (DPI), project 776n.

Author Contributions A.H.G. and D.J.M. designed the experiments. A.H.G. studied the macroscopic deformations and analysed the results. D.J.M. synthesized I. G.V. synthesized II. M.V. and A.K. developed the theoretical model. D.J.B. supervised the overall research. E.W.M. participated in the interpretation of the results. R.L.B.S. supervised the theoretical modelling. All authors contributed to the writing of the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations. Correspondence and requests for materials should be addressed to D.J.B. (D.Broer@tue.nl; experiments) or R.L.B.S. (rselinge@kent.edu; theory).

Reviewer Information Nature thanks T. Ikeda, R. Verduzco and Y. Yu for their contribution to the peer review of this work.
METHODS

Synthesis of azopyridine (AzoPy), precursor of I. See Extended Data Fig. 1 for the chemical structures. 4-(4-hydroxyphenylazo)pyridine (ii), 4-(4-hydroxyphenylazo)pyridine (ii) was prepared according to the procedure described in ref. 26.

H NMR (400 MHz, D2O): δ (p.p.m.) = 10.64 (s, OH, 1H), 8.75 (d, J = 6 Hz, 2H), 7.86 (d, J = 9 Hz, 2H), 7.66 (dd, J = 6 Hz, 7 Hz, 2H, 6.98 (dd, J = 9 Hz, 2H, 2H).

C NMR (100 MHz, D2O): δ (p.p.m.) = 162.76, 157.28, 151.72, 145.71, 126.24, 116.65, 116.26.

overnight. The mixture was cooled, filtered and concentrated under vacuum.

J 7.73 (d, J = 7 Hz, 2H), 3.14 (t, J = 7 Hz, 2H, 1H), 1.94 (p, J = 7 Hz, 2H, 7.10 (p, J = 7 Hz, 2H), 1.45 (m, 4H).

C NMR (100 MHz, CDCl3): δ (p.p.m.) = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46, 27.80, 25.20, 18.33.

IR (ATR): νmax = 3084, 1676, 1507, 1450, 1219, 1039, 832, 792, 713, 660, 592 cm−1.

Synthesis of azopyridine (AzoPy), precursor of I. 6-bromohexyl methacrylate (iii), 6-bromohexyl methacrylate (iii) was prepared according to the procedure described in ref. 27. except that here acryloyl chloride was replaced by methacyryloyl chloride.

H NMR (400 MHz, CDCl3): δ (p.p.m.) = 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, J = 7 Hz, 2H, 2H, 3.14 (t, J = 7 Hz, 2H, 1H), 1.94 (p, J = 7 Hz, 2H, 7.10 (p, J = 7 Hz, 2H), 1.45 (m, 4H).

C NMR (100 MHz, CDCl3): δ (p.p.m.) = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46, 27.80, 25.20, 18.33.

IR (ATR): νmax = 3084, 1676, 1507, 1450, 1219, 1039, 832, 792, 713, 660, 592 cm−1.

H NMR (400 MHz, CDCl3): δ (p.p.m.) = 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, J = 7 Hz, 2H, 2H, 3.14 (t, J = 7 Hz, 2H, 1H), 1.94 (p, J = 7 Hz, 2H, 7.10 (p, J = 7 Hz, 2H), 1.45 (m, 4H).

C NMR (100 MHz, CDCl3): δ (p.p.m.) = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46, 27.80, 25.20, 18.33.

IR (ATR): νmax = 3084, 1676, 1507, 1450, 1219, 1039, 832, 792, 713, 660, 592 cm−1.

H NMR (400 MHz, CDCl3): δ (p.p.m.) = 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, J = 7 Hz, 2H, 2H, 3.14 (t, J = 7 Hz, 2H, 1H), 1.94 (p, J = 7 Hz, 2H, 7.10 (p, J = 7 Hz, 2H), 1.45 (m, 4H).

C NMR (100 MHz, CDCl3): δ (p.p.m.) = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46, 27.80, 25.20, 18.33.

IR (ATR): νmax = 3084, 1676, 1507, 1450, 1219, 1039, 832, 792, 713, 660, 592 cm−1.

H NMR (400 MHz, CDCl3): δ (p.p.m.) = 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, J = 7 Hz, 2H, 2H, 3.14 (t, J = 7 Hz, 2H, 1H), 1.94 (p, J = 7 Hz, 2H, 7.10 (p, J = 7 Hz, 2H), 1.45 (m, 4H).

C NMR (100 MHz, CDCl3): δ (p.p.m.) = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46, 27.80, 25.20, 18.33.

IR (ATR): νmax = 3084, 1676, 1507, 1450, 1219, 1039, 832, 792, 713, 660, 592 cm−1.

H NMR (400 MHz, CDCl3): δ (p.p.m.) = 6.10 (s, 1H), 5.55 (s, 1H), 4.15 (t, J = 7 Hz, 2H, 2H, 3.14 (t, J = 7 Hz, 2H, 1H), 1.94 (p, J = 7 Hz, 2H, 7.10 (p, J = 7 Hz, 2H), 1.45 (m, 4H).

C NMR (100 MHz, CDCl3): δ (p.p.m.) = 167.47, 136.46, 125.24, 64.52, 33.68, 32.62, 28.46, 27.80, 25.20, 18.33.

IR (ATR): νmax = 3084, 1676, 1507, 1450, 1219, 1039, 832, 792, 713, 660, 592 cm−1.
The rate of change that we selected for $S$ enables full transition in less than 1 s in each direction. The effective force on each node is calculated as the derivative of the total potential energy with respect to node displacement. Every node experiences an effective force contribution from each tetrahedral element it touches, and these are summed vectorwise at each time step. Node equations of motion are integrated using the velocity Verlet algorithm, with new forces calculated at each time step, while clamped nodes at the ends of the film are held fixed. The optics calculation to determine which parts of the top surface of the film are illuminated is also repeated at each time step.

The substrate below the film is modelled as an infinitely hard and smooth surface, and collisions between the film and the substrate are treated as inelastic. Dissipative forces proportional to node momentum are added to approximate the effects of air resistance. The finite-element simulation suggests that kinetic energy plays a key part in the shape response. If we increase the amount of dissipation (drag) in the finite-element simulation above a threshold value, then wave motion fails to initiate.

The simulation code is implemented for GPU acceleration. Using a time step of $2 \times 10^{-5}$ s, $2 \times 10^{6}$ time steps requires about 25 min to execute on a single GPU-equipped processor, modelling a total of 40 s of motion.

The finite-element model does not take into consideration the temperature dependence of the elastic moduli of the material or the effects of thermal expansion. These effects may be explored in more detailed modelling efforts in the future, but the present simulation demonstrates that they are not essential for generating perpetual wave motion.

**Data availability.** The datasets generated and analysed during this study are available from the corresponding authors on reasonable request.

26. Naidek, K. P. et al. Ruthenium acetate cluster amphiphiles and their Langmuir-Blodgett films for electrochromic switching devices. *Eur. J. Inorg.* Chem. 2014, 1150–1157 (2014).
27. Stumpel, J. E., Liu, D., Broer, D. J. & Schenning, A. P. H. J. Phot-switchable hydrogel surface topographies by polymerisation-induced diffusion. *Chem. Eur. J.* 19, 10922–10927 (2013).

© 2017 Macmillan Publishers Limited, part of Springer Nature. All rights reserved.
Extended Data Figure 1 | Synthetic routes for constituent compounds. Components of the LCN films include AzoPy, I and II.
Extended Data Figure 2 | Thermal characterization of the mixtures used in the study. 

a. Differential scanning calorimetry scans (second runs, exotherm downwards) showing the phase behaviour of all mixtures investigated. The nematic-to-isotropic transition occurs at 90 °C.

b. Differential scanning calorimetry scan of a polymerized sample showing the change in specific heat at the glass transition temperature ($T_g$). The table summarizes the $T_g$ data of the various polymerized compositions.

c. Normalized absorption spectra of the various mixtures investigated.

|       | LCN I | LCN II | DR1A | AzoPy | AEMA |
|-------|-------|--------|------|-------|------|
| $T_g$ | 50.2  | 51.3   | 51.7 | 50.7  | 53.9 |
Extended Data Figure 3 | Relaxation kinetics of the azo-derivatives embedded in the LCN. a–d. Thermal relaxation from the photostationary cis state to the trans state of A6MA (a), I (b), II (c) and DR1A (d) at various temperatures. Here $\Delta A = \frac{A(t) - A_{\infty}}{A_{\infty} - A_0}$ and $A(t) = (A_{\infty} - A_0)e^{(-\Delta t/\beta)} + A_{\infty}$. © 2017 Macmillan Publishers Limited, part of Springer Nature. All rights reserved.
Extended Data Figure 4 | Pictures taken at different angles showing the curvatures that were created, inducing the self-shadowing effect. Scale bar, 5 mm. At 90°, the bump is formed (indicated by the arrow), but because no shadow is created the wave cannot propagate and the film remains in that position.
Extended Data Figure 5 | Temperature measured at the front of the wave. a, Influence of the intensity on the temperature increase at the front of the wave. The red shaded region is a guide to help to visualize the glass transition region. b, Measured temperature for the uniaxially oriented sample. Despite the rubbery character of the films, no motion was observed.
Extended Data Figure 6 | Temperature measurements during wave propagation. 

**a, c.** Thermal pictures of the wave taken at different times t. 

**b.** Temperature profile over the length of the film (along the black line in **a**) for the homeotropic-up sample during wave propagation at t = 0 s (black line), t = 0.67 s (dark grey line) and t = 1.40 s (light grey line).

**d.** Temperature profiles over the length of the film (along the black line in **c**) for the planar-up sample at t = 0 s (black line), t = 0.11 s (dark grey line) and t = 0.22 s (light grey line).
Extended Data Figure 7 | $^1$H NMR spectra of the constituent compounds. a, $^1$H NMR of the compound AzoPy, which was used to form compound I. b, $^1$H NMR of compound II.
Extended Data Figure 8 | Transmission spectra of the LCN films.
Transmissions (T, expressed as percentages) for compound I (green), compound II (black), A6MA (red), AzoPy (pink) and DR1A (blue) are shown. Thickness, 20 μm. The films containing A6MA, compound I and AzoPy are actuated with 405-nm light. At this wavelength, the transmissions are 6.3%, 4.1% and 8.9%, respectively. The samples containing DR1A and compound II are illuminated with 455-nm light. At this wavelength, the initial transmissions are 26% and 13%, respectively.
### Extended Data Table 1 | Chemical compositions of the mixtures

| Compound     | Mixture with AzoPy | Mixture with Compound I | Mixture with Compound II | Mixture with A6MA | Mixture with DR1A |
|--------------|---------------------|-------------------------|--------------------------|------------------|------------------|
| AzoPy        | 7 mol %             | /                       | /                        | /                | /                |
|              | 5 mg                |                         |                          |                  |                  |
| Compound I   | /                   | 7 mol %                 | /                        | /                | /                |
|              | /                   | 9 mg                    |                          |                  |                  |
| Compound II  | /                   | /                       | 7 mol %                  | /                | /                |
|              | /                   | /                       | 7 mg                     |                  |                  |
| A6MA         | /                   | /                       | /                        | 7 mol %          | /                |
|              | /                   | /                       | /                        | 7 mg             | /                |
| DR1A         | /                   | /                       | /                        | /                | 1 mol %          |
|              | /                   | /                       | /                        | /                | 1 mg             |
| RM82         | 57 mol %            | 50 mol %                | 50 mol %                 | 51 mol %         | 57 mol %         |
|              | 70 mg               | 61 mg                   | 63 mg                    | 63 mg            | 70 mg            |
| RM23         | 35 mol %            | 42 mol %                | 41 mol %                 | 41 mol %         | 41 mol %         |
|              | 25 mg               | 30 mg                   | 30 mg                    | 30 mg            | 29 mg            |
| Irgacure 819 | 1 mol %             | 1 mol %                 | 1 mol %                  | 1 mol %          | 1 mol %          |
|              | 1 mg                | 1 mg                    | 1 mg                     | 1 mg             | 1 mg             |

The mixture containing DR1A has a slightly different composition (lower molar percentage of dye) because the extinction coefficient of DR1A is higher than the other molecules. Consequently, the amounts of RM23 and RM82 are also adjusted to maintain a similar quantity of cross-linker. Both the molar ratio (mol%) and the corresponding amount (mg) are reported.