

Mastering the photothermal effect in liquid crystal networks

Citation for published version (APA):

Gelebart, A. H., Vantomme, G., Meijer, E. W., & Broer, D. J. (2017). Mastering the photothermal effect in liquid crystal networks: a general approach for self-sustained mechanical oscillators. *Advanced Materials*, 29(18), [1606712]. <https://doi.org/10.1002/adma.201606712>

DOI:

[10.1002/adma.201606712](https://doi.org/10.1002/adma.201606712)

Document status and date:

Published: 10/05/2017

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Mastering the Photothermal Effect in Liquid Crystal Networks: A General Approach for Self-Sustained Mechanical Oscillators

Anne Helene Gelebart, Ghislaine Vantomme, E. W. Meijer,* and Dirk J. Broer*

Chemical networks and molecular switches dominate the area of research geared toward macroscopic motion of materials. A counter-intuitive approach to create self-sustained oscillation by light irradiation of ordinary photostabilizers in splay-aligned liquid-crystalline networks made from commercial mesogens is developed. Photostabilizers or any molecules that are able to quickly dissipate the absorbed light through heat, by vibrational and/or rotational modes, can reach self-oscillating macroscopic motion where self-shadowing plays a critical role. The mechanical self-oscillation is linked to temperature oscillations and the asymmetric response over the film thickness. Only a localized responsive zone, acting as hinge, activates the oscillation of a beam-shaped device. The outcome of this research is extended from UV to near-IR actuation, making bulk applications to convert sunlight into mechanical work within reach.

The field of molecular machinery holds revolutionary promises for the future of our society as illustrated by the 2016 Nobel Prize in Chemistry being awarded to Jean-Pierre Sauvage, Fraser Stoddart, and Ben Feringa for their pioneering work on the design and synthesis of molecular machines. They incorporated mechanical bonds and unidirectional rotatory units into functional molecular machineries to control motion and function of nanomotors. Connecting these molecular machines to the macroscopic world is a next challenge where the work performed at the molecular scale is translated to the production of desired operations in functional devices. Only few examples are reported of translating the out-of-equilibrium state of molecules to achieve continuous macroscopic motion of materials.^[1–10] Most of them use the well-known Belousov–Zhabotinsky reaction which, when coupled to an adaptive gel, achieves continuous chemical waves through the gel.^[2] Recently, synthetic homeostatic materials with chemo-mechanochemical self-regulation have been disclosed,

A. H. Gelebart, Dr. G. Vantomme, Prof. E. W. Meijer, Prof. D. J. Broer
Institute for Complex Molecular Systems
Eindhoven University of Technology
PO Box 513, 5600 MB, Eindhoven, The Netherlands
E-mail: e.w.meijer@tue.nl; d.broer@tue.nl



This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

DOI: 10.1002/adma.201606712

showing another unique way of obtaining self-oscillating materials.^[5,6] Also, light has attracted much attention because of the high spatial and temporal precisions offered. For the purpose of creating these light-sensitive materials, the design and synthesis of molecules that can undergo reversible switching between *trans*–*cis* and opened–closed isomers have received considerable attention.^[8–16]

Typically such a photoswitch is integrated in various amounts in a gel, elastomer, crystal, or liquid crystal network (LCN).^[17] The latter has the advantage of intrinsic anisotropy that predefines the deformation of the material at hand.^[18] Usually the *trans*–*cis* isomerization of azobenzene units is used as the molecular trigger, since its geometrical change at

the molecular level is translated to a significant macroscopic motion.^[18–23] Recently, interest moves beyond azobenzene-based systems with exciting examples using diarylethenes,^[24] twisted alkenes,^[16] and rotaxanes.^[25] A few out-of-equilibrium examples in LCNs are presented in which a constant light irradiation is capable of inducing continuous macroscopic motion.^[8,9,26–31] In particular, the group of White reported a cantilever that self-oscillates with large amplitude under constant light irradiation and proposed a mechanism based on reorientation of the mesogens upon illumination of the azobenzenes with polarized light.^[30,31] The different classes of switching molecules are interesting for their versatility, allowing tuning of their isomerization kinetics and/or absorption. However, all those molecules offer real challenges when to become integrated in consumer-based products, with issues related to fatigue, synthetic accessibility, limited kinetics in both directions, photobleaching, etc.

Here we demonstrate a very simple and counter-intuitive approach to construct simple materials that show a steady self-oscillation. Thereto we use the mechanism of ordinary photostabilizers to create a photothermal effect in a splay-aligned LCN made from commercial reactive mesogens. Usually, photostabilizers are added to a polymer in order to prevent ageing, color change, or delamination of coatings by converting the absorbed light into heat through vibrational and rotation modes.^[32] Despite their extensive use in the industry of bulk polymers, photostabilizers have never been investigated to induce deformation nor oscillations in materials. We chose to incorporate photostabilizers in reactive mesogens; both are commercially available and broadly used in the chemical industry (Figure 1). We selected

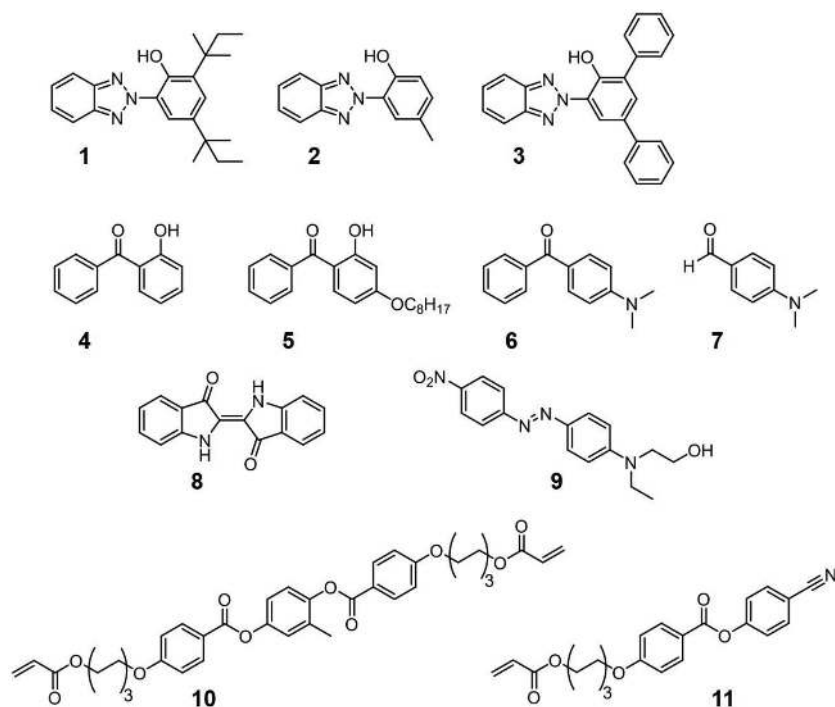


Figure 1. Chemical structures used. Structures of the photostabilizers and dyes 1–9 incorporated in commercially produced reactive mesogens 10–11 to obtain self-oscillating liquid-crystalline polymer films by photopolymerization.

(hydroxyphenyl)benzotriazoles 1–3, benzophenones 4–6,^[33–36] and dimethylaminobenzaldehyde 7. The validity of the model was extended to the full visible range by using commercial dyes such as indigo 8^[37] and red disperse 9, molecules that are known for conformational changes upon excitation. The LCNs are made from the nematic acrylate and diacrylate mesogens 10 and 11. A small amount of stabilizers (or dye) incorporated in the LCN is sufficient (≥ 1 wt%) to observe steady self-oscillation.

LCNs were easily prepared by the photocopolymerization of LC monomers 10 and 11 aligned in a splay configuration as shown in Figure 2a.^[38–40] The splay alignment consists of a gradual change in the director of the LC through the thickness of the film going from planar to homeotropic. Upon actuation, it results a contraction at the planar side and an expansion at the homeotropic side of the film, which induces a tight bending due to a difference in expansion/shrinkage between the two sides of the film with relatively small changes of the order parameter. Initially, photostabilizer 1 (Tinuvin) was used. Thin transparent films (20 μm) were obtained and cut in strips (1.7 cm \times 0.4 cm). Thin films were used to minimize light intensity gradients due to absorption, which ensures dye excitation at both sides of the film promoting a large deformation. Also, from mechanical considerations, the deformation of thinner films is larger for a given input of light. The film was clamped at one side and showed natural bending with the homeotropic alignment in the center of the curvature. This prebending at the resting state is due to residual stresses originating from the polymerization process. When this film was exposed to a light-emitting diode (LED) (365 nm and ≥ 450 mW cm^{-2}), bending of the film toward the light was observed, followed by

a continuous oscillation of the polymer strip, as shown in the sequence in Figure 2b and in Movie S1 (Supporting Information). The frequency of the oscillation was 6.3 ± 0.3 Hz and the amplitude, defined as the displacement in the z -direction of the tip reached 8 mm. This mechanical self-oscillation was accompanied by thermal oscillation of the film (Figure 2c). The self-oscillating motion was constant over more than one hour (Figure 2e), showing high stability and little fatigue of the system within the error range. The main issue for the ageing of the thin film is its brittleness that can be circumvent by tuning the crosslink density. One should emphasize that the use of a collimated light beam is crucial to enter in the self-sustained oscillation regime. A diffuse source leads to bending of the whole film with a deformation pattern similar as the ones reported previously, e.g., by using a heat source.^[40]

Classical mechanics can be used to explain the frequency of the oscillation observed. The natural frequency f of a cantilever beam subjected to free vibrations is given by:

$$f = \frac{\alpha^2}{2\pi} \sqrt{\frac{EI}{mL^4}} \quad (1)$$

with I and m defined as,

$$I = \frac{\text{width} \times \text{thickness}^3}{12} \quad m = \rho \times \text{width} \times \text{thickness} \quad (2)$$

In the above equation, $\alpha = 1.875$ is a constant dependent on the mode of oscillation. E represents the apparent tensile modulus and depends on the film temperature (Figures S1 and S2, Supporting Information). I represents the moment of inertia of the LCN film and m corresponds to the mass per length unit. The volume mass ρ of a LCN is known to be $1.22 \cdot 10^3$ kg m^{-3} ^[41] and finally L corresponds to the length of the film. With an average temperature of the film of 57 $^\circ\text{C}$ (Figure 2c), the frequency calculated with Equation (1) is 5.9 Hz, giving a good agreement between the theoretical and the experimental data. The increase in temperature is consistent for every sample giving raise to oscillation. A series of reference experiments was performed to understand the role of the absorbed photons and their conversion into heat. In one experiment, the dopant anthracene was incorporated in the LCN. It absorbed light but released the energy by fluorescence, which induces a limited increase of temperature (only few degrees). In another experiment, we employed an azobenzene dye with a slow *cis* to *trans* back isomerization. Slow relaxation leads to a photostationary equilibrium state where the *cis* isomer is predominant. In both cases, a stationary bent state of the film was produced in the absence of heat dissipation in the photochemical process. It suggests that the transfer of photons into radiation-less de-excitation and/or a fast dynamics within the system is needed to achieve sufficient heat.

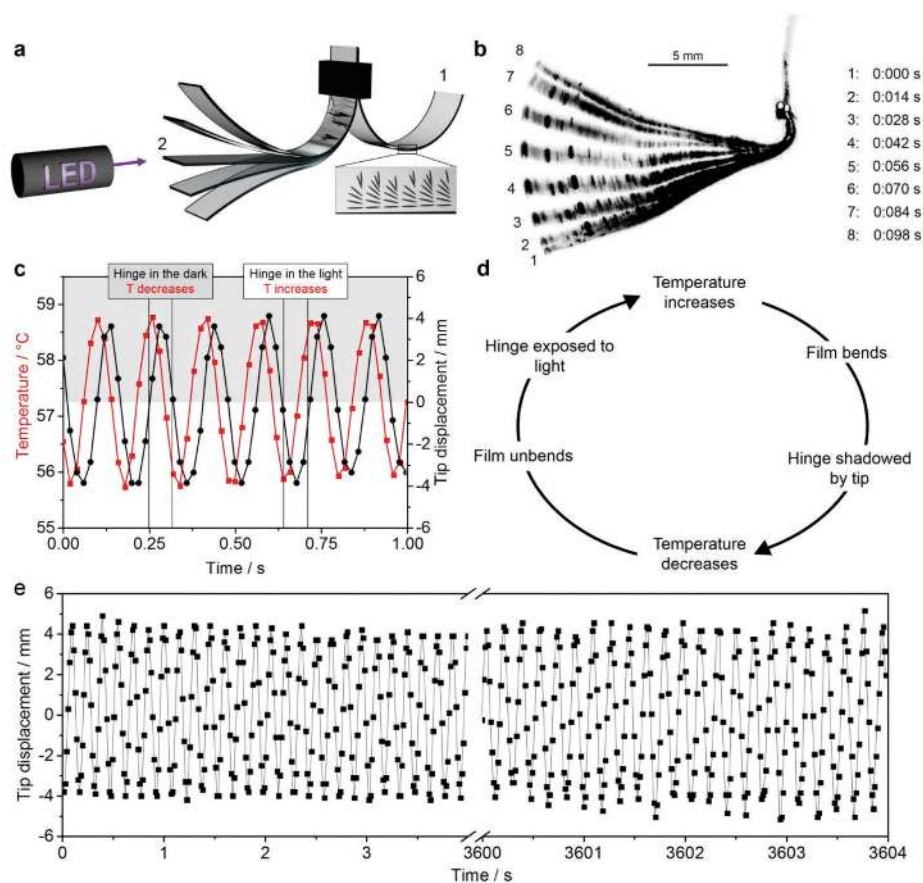


Figure 2. Steady light-induced self-oscillation of a film. a) Schematic representation of the setup and the splay alignment (inset). Initially the film is curved (position 1). When the light is switched on, the film bends toward the light (position 2) where it starts oscillating. b) Overlay of frames showing oscillation of the film containing the stabilizer **1**, irradiated from the left with UV light (LED 365 nm, 0.52 W cm^{-2}). The film geometry is $1.7 \text{ cm (l)} \times 0.4 \text{ cm (w)} \times 20 \mu\text{m (th)}$. c) Thermal (red trace) and mechanical (black trace) oscillations of the film measured at the exposed spot (hinge). d) The feedback loop created by the self-shadowing. e) Displacement of the film tip over time in the z-direction.

During irradiation, thermal oscillations with an amplitude of about $2\text{--}3 \text{ }^\circ\text{C}$ and a frequency matching the mechanical oscillation were observed due to self-shadowing of the film (Figure 2c and Movie S2, Supporting Information). We propose that the mechanism of oscillation goes as followed: when the light hits a spot on the film (the hinge), the temperature locally increases due to photothermal excitation of the dopants. The internal heat induces thermal expansion at the light spot governed by the molecular alignment and results in a film bending at the hinge.^[42] The film moves in such a way that its tip starts to shadow its hinge. This self-shadowing effect subsequently decreases the film temperature. While the hinge cools down, the film unbends to its resting position placing the hinge in the light beam and repeating again the described sequence (Figure 2d). The film keeps moving upward while the tip already shadows the hinge, we assume that this delay is due to the inertia gained during the actuation. Similarly, the film keeps going down while the hinge is in the light. An interplay between the constant input of light (to trigger and maintain the motion), the inertia of the film, and the elastic properties (constantly act to bring the film to its rest position) are the key parameters involved in the steady oscillation. To confirm that oscillation of $2\text{--}3 \text{ }^\circ\text{C}$ amplitude of temperature by self-shadowing is plausible,

a constrained film was irradiated with a strobe light of frequency 6 Hz and showed similar range of temperature variation (Figure S3, Supporting Information).

The above makes the system very general and this generality is shown with the successful incorporation of a large series of photostabilizers and dyes into the LCN to arrive at steady self-oscillations. The molecules used differ in their excitation wavelengths (from 365 to 600 nm) and their mechanisms of conversion of light into vibrational and/or rotational energy. The transformation of the light energy into dissipative heating by intramolecular proton transfer is well described for the stabilizers **1–5**.^[33–36] Stabilizers **1–6** do not absorb in the visible range, which has the advantage to give colorless and transparent films and broaden the field of applications. Interestingly, films of the same dimensions irradiated with light at the excitation wavelength of the stabilizers (365 nm for the (hydroxyphenyl) benzotriazoles **1–3** and the benzophenones **4–6**, 405 nm for the benzaldehyde derivative **7**, and white light for indigo **8** and red for disperse **9**) gave oscillation of the same frequency within the error range (Figure 3a). It shows that the motion depends on the intrinsic mechanical properties of the LCN only and not on the molecular resonator. Thus, the oscillation frequency can be tuned by changing the film dimensions or adjusting the film

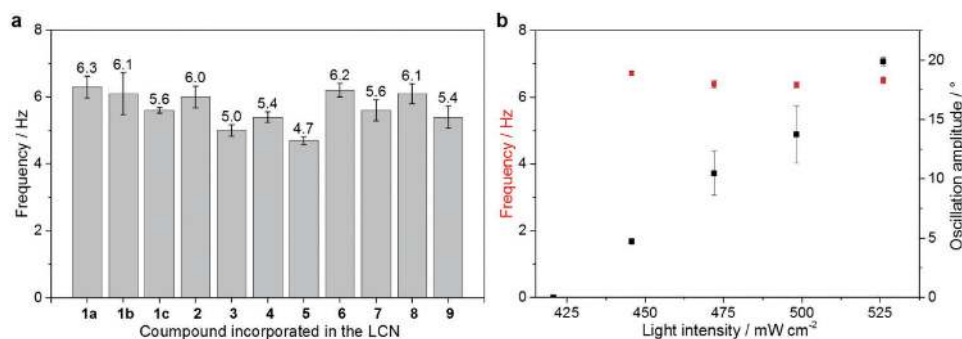


Figure 3. Frequency and amplitude of the oscillation with various dopants. a) Oscillation frequency of the films containing different photostabilizers and dyes. The geometry of the film is 1.7 cm (l) × 0.4 cm (w) × 20 μm (th). Components 1a, 1b, and 1c correspond respectively to 5, 2.5, and 1 wt% of photostabilizer 1 added in the LCN. b) Frequency (red dots) and amplitude (black dots) as a function of light intensity. The error bars were obtained by repeating the measures on three strips taken from different films. The mean is plotted and the error bars represent the standard deviation.

composition, i.e., changing the crosslink density or the spacer length to alter the modulus.

To verify further that the frequency is solely dependent on the dimensional and mechanical properties of the film, we showed its independency of the concentration of photostabilizer and light intensity (Figure 3). Quantities lower than 1 wt% yielded only bending similar to earlier report.^[40] Addition of more than 10 wt% induced disorder into the LC splay alignment and less controlled deformation. Most remarkable, the amplitude depends on the intensity of the incident light and not on the concentration of active component. We speculate that by increasing the light intensity, the system receives more energy released via larger oscillation amplitude. It also means that in the concentration regime used, almost all the light is absorbed through the thickness of the film. Moreover,

the average temperature of the film does not vary significantly during irradiation with different light intensities (see Figure S4, Supporting Information), this can be related to energy balance where light-induced heat is converted into mechanical energy upon bending including the (visco-)elastic forces and air drag.

The limits of technical usability of this general system are explored by using a film containing only a narrow line of active component. Indigo as active component enables sunlight as the trigger (Figure 4a). The film was clamped on one side and placed into the beam of focus sunlight (Figure 4b). The film bent precisely and solely at the position of the indigo creating a hinge restricted to a confined area (Figure 4d). By tuning the angle of incidence of the sunlight in order to have a self-shadowing effect, the film continuously oscillated with a frequency of 6.8 ± 0.2 Hz and an amplitude of $21^\circ \pm 3^\circ$ (Figure 4c and

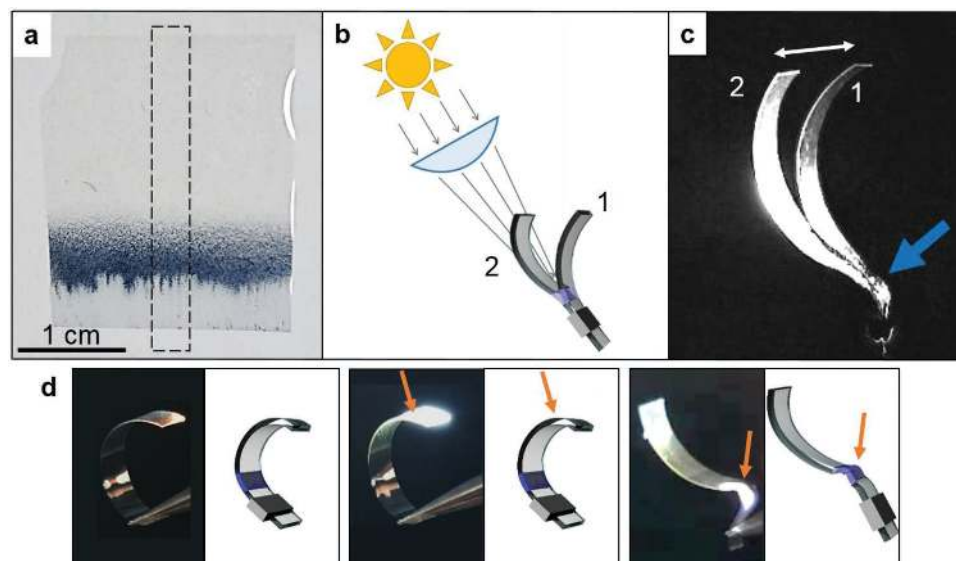


Figure 4. Self-oscillation obtained with the indigo hinge. a) Picture of the nonactive film with the hinge of indigo component. b) Schematic representation of the setup used to actuate the LCN film containing a stripe of indigo. The sunlight is focused by a lens and has sufficient intensity to bring the system into an oscillating mode, between positions 1 and 2. c) Superposition of two pictures of the oscillating film in positions 1 and 2. Over time, the film is moving continuously between these two positions. The self-shadowing at the hinge is visible in this superposition. In position 1 the hinge is in the shadow whilst it is in the sunlight in position 2. d) In the first picture, the film is in the dark at the resting state. In the second picture, the focus point of the light (indicated by the orange arrow) does not overlap with the indigo stripe and no bending is observed. In the last picture, the film is positioned so that the focused light reaches the indigo stripe. In that condition only, the film bends significantly and self-oscillates.

Movie S3, Supporting Information). It indicates that molecular photoexcitation at the precise spot of irradiation is sufficient to induce global self-oscillation of the film.

In conclusion, we disclose that molecules capable of transferring light energy into heat are suitable dopants to induce actuation, and more importantly, oscillation of LCNs. With this study, we offer a general approach to create light-responsive devices using commercially accessible materials. The light-sensitive components have a proven record as photostabilizers or dyes, and are therefore more durable than any other previously studied photoswitching molecule. This not only opens durable outdoor solutions for applications in soft robotics and automated systems formally rejected because of fatigue of the photoactive component, but also provides new direction for the emerging area of extreme mechanics.^[43,44]

Experimental Section

The reactive mesogens **10** and **11** were obtained via Merck. The photoinitiator Irgacure 819 and the Tinuvin **1** were purchased from Ciba. Compounds **2–9** were purchased from Aldrich. Light irradiation was carried out with collimated LEDs from Thorlabs. The movies were recorded on a PCO 5.5 sCMOS camera. The surface temperature of the films was reported with a high speed thermal camera Gobi from Xenics.

Differential scanning calorimetry (DSC) data were collected on a DSC Q1000 from TA instruments and calibrated with an indium standard. The sample was subjected to two cooling/heating cycles from -30 to 130 °C with a rate of 10 °C min^{-1} . The storage modulus of the films was determined using a Q800 machine by TA Instruments.

The mixtures were prepared by dissolution in dichloromethane of the different molecules used in the following ratio: 65 wt% of **10**, 30 wt% of **11**, 5 wt% of the photostabilizer or dye, and <1 wt% of Irgacure 819. The solvent was subsequently evaporated.

Cells were made by gluing together two glass plates coated with a homeotropic alignment layer (PI Al 1051 purchased from Nissan) at the top and a planar alignment layer (PI 5300 purchased from Sunever) at the bottom. Prior gluing, the planar alignment layer was rubbed in order to obtain monodomain alignment throughout the whole sample. Glass beads with a diameter of 20 μm were used to precisely control the gap of the cell.

The cells were filled with the liquid-crystalline mixture in the isotropic phase (100 °C) and cooled down to reach the nematic phase (70 °C). The photopolymerization was carried out by irradiation at 455 nm for about 40 min followed by a thermal postcuring at 130 °C for 10 min.

To prepare the film containing only a hinge of the active material indigo, the filling was split in three steps, using two mixtures prior to polymerization. The mixture **1** consisted of the mesogens **10** and **11** only while the mixture **2** contained additionally the indigo. The cell was successively filled with (1) the mixture **1** until $2/3$ of the cell length, (2) the mixture **2** in 2 mm of the cell length, and (3) the mixture **1** until complete filling.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.H.G. and G.V. contributed equally to this work. This work was financially supported by the Netherlands Organization for Scientific

Research (NWO—TOP PUNT Grant: 10018944) and the European Research Council (Vibrate ERC, Grant 669991). A.H.G. acknowledges the funding from the People Program (Marie Curie Actions) of the European Union's Seventh Framework Program FP7-2013, Grant No. 607602.

Received: December 12, 2016

Revised: January 16, 2017

Published online: February 22, 2017

- [1] G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418.
- [2] M. L. Smith, C. Slone, K. Heitfeld, R. A. Vaia, *Adv. Funct. Mater.* **2013**, *23*, 2835.
- [3] R. Tamate, A. Mizutani Akimoto, R. Yoshida, *Chem. Rec.* **2016**, *16*, 1852.
- [4] T. Masuda, M. Hidaka, Y. Murase, A. M. Akimoto, K. Nagase, T. Okano, R. Yoshida, *Angew. Chem. Int. Ed.* **2013**, *52*, 7468.
- [5] P. Dayal, O. Kuksenok, A. C. Balazs, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 431.
- [6] X. He, M. Aizenberg, O. Kuksenok, L. D. Zarzar, A. Shastri, A. C. Balazs, *Nature* **2012**, *487*, 214.
- [7] H. Arazoe, D. Miyajima, K. Akaike, F. Araoka, E. Sato, T. Hikima, M. Kawamoto, T. Aida, *Nat. Mater.* **2016**, *15*, 1084.
- [8] T. Ikegami, Y. Kageyama, K. Obara, S. Takeda, *Angew. Chem. Int. Ed.* **2016**, *55*, 8239.
- [9] E. Uchida, R. Azumi, Y. Norikane, *Nat. Commun.* **2015**, *6*, 7310.
- [10] M. K. Panda, T. Runčevski, A. Husain, R. E. Dinnebie, P. Naumov, *J. Am. Chem. Soc.* **2015**, *137*, 1895.
- [11] G. S. Kumar, D. C. Neckers, *Chem. Rev.* **1989**, *89*, 1915.
- [12] T. I. Y. Zhao, *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals*, Wiley, Hoboken, NJ, USA, **2009**.
- [13] H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.* **2012**, *41*, 1809.
- [14] M. Dong, A. Babalhavaejji, S. Samanta, A. A. Beharry, G. A. Woolley, *Acc. Chem. Res.* **2015**, *48*, 2662.
- [15] Z. Yu, S. Hecht, *Chem. Commun.* **2016**, *52*, 6639.
- [16] N. Koumura, R. W. Zijlstra, R. A. van Delden, N. Harada, B. L. Feringa, *Nature* **1999**, *401*, 152.
- [17] D. Liu, D. J. Broer, *Langmuir* **2014**, *30*, 13499.
- [18] L. T. de Haan, A. P. H. J. Schenning, D. J. Broer, *Polymer* **2014**, *55*, 5885.
- [19] E. Merino, M. Ribagorda, *Beilstein J. Org. Chem.* **2012**, *8*, 1071.
- [20] A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139.
- [21] P. K. Kundu, R. Klajn, *ACS Nano* **2014**, *8*, 11913.
- [22] Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145.
- [23] X. Qing, L. Qin, W. Gu, Y. Yu, *Liq. Cryst.* **2016**, *43*, 1.
- [24] M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172.
- [25] B. K. Juluri, A. S. Kumar, Y. Liu, T. Ye, Y.-W. Yang, A. H. Flood, L. Fang, J. F. Stoddart, P. S. Weiss, T. J. Huang, *ACS Nano* **2009**, *3*, 291.
- [26] K. Kumar, C. Knie, D. Bléger, M. A. Peletier, H. Friedrich, S. Hecht, D. J. Broer, M. G. Debije, A. P. H. J. Schenning, *Nat. Commun.* **2016**, *7*, 11975.
- [27] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, *Nat. Mater.* **2004**, *3*, 307.
- [28] A. Kausar, H. Nagano, T. Ogata, T. Nonaka, S. Kurihara, *Angew. Chem. Int. Ed.* **2009**, *48*, 2144.
- [29] M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem. Int. Ed.* **2008**, *47*, 4986.
- [30] T. J. White, N. V. Tabiryan, S. V. Serak, U. A. Hrozhyk, V. P. Tondiglia, H. Koerner, R. A. Vaia, T. J. Bunning, *Soft Matter* **2008**, *4*, 1796.
- [31] K. M. Lee, M. L. Smith, H. Koerner, N. Tabiryan, R. A. Vaia, T. J. Bunning, T. J. White, *Adv. Funct. Mater.* **2011**, *21*, 2913.
- [32] M. Zayat, P. Garcia-Parejo, D. Levy, *Chem. Soc. Rev.* **2007**, *36*, 1270.

- [33] J. Keck, H. E. A. Kramer, H. Port, T. Hirsch, P. Fischer, G. Rytz, *J. Phys. Chem.* **1996**, *100*, 14468.
- [34] M. J. Paterson, M. A. Robb, L. Blancafort, A. D. DeBellis, *J. Am. Chem. Soc.* **2004**, *126*, 2912.
- [35] A. Maliakal, G. Lem, N. J. Turro, R. Ravichandran, J. C. Suhadolnik, A. D. DeBellis, M. G. Wood, J. Lau, *J. Phys. Chem. A* **2002**, *106*, 7680.
- [36] H. J. Heller, H. R. Blattmann, *Pure Appl. Chem.* **1973**, *36*, 141.
- [37] T. Kobayashi, P. M. Rentzepis, *J. Chem. Phys.* **1979**, *70*, 886.
- [38] D. J. Broer, G. N. Mol, *Polym. Eng. Sci.* **1991**, *31*, 625.
- [39] C. L. van Oosten, C. W. M. Bastiaansen, D. J. Broer, *Nat. Mater.* **2009**, *8*, 677.
- [40] C. L. van Oosten, K. D. Harris, C. W. M. Bastiaansen, D. J. Broer, *Eur. Phys. J. E* **2007**, *23*, 329.
- [41] D. Liu, C. W. M. Bastiaansen, J. M. J. den Toonder, D. J. Broer, *Macromolecules* **2012**, *45*, 8005.
- [42] G. N. Mol, K. D. Harris, C. W. M. Bastiaansen, D. J. Broer, *Adv. Funct. Mater.* **2005**, *15*, 1155.
- [43] D. Yang, B. Mosadegh, A. Ainla, B. Lee, F. Khashai, Z. Suo, K. Bertoldi, G. M. Whitesides, *Adv. Mater.* **2015**, *27*, 6323.
- [44] W. J. Duncanson, T. E. Kodger, S. Babae, G. Gonzalez, D. A. Weitz, K. Bertoldi, *Langmuir* **2015**, *31*, 3489.