



Beam steering by Liquid Crystalline Elastomer Fibres

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The problem of addressing a laser beam as information vehicle into different channels is an open problem in the telecommunication field. Switching of a signal into different ports has been demonstrated, to date, employing complex devices and mechanisms as the electro optic effect, MEMS mirrors or liquid crystal based spatial light modulators (SLMs). We present here a simple device, namely a mirror held by a Liquid Crystal Elastomer (LCE) fibre, as an optically and remotely driven beam steerer. In fact, a considered signal (laser beam) can be addressed in every in-plane direction, by controlling the fibre and mirror rotation, i.e. the deflected probe beam angle. Such movement is possible thanks to the preparation of LCE fibres able to rotate and contract under a selective light stimulus. By adjusting the irradiation stimulus power, elastic fibres are able to rotate with a specific angle performing more than one complete revolution around their axis. The described movement is perfectly reversible as soon as the stimulus is removed.

Introduction

Conversion of light into mechanical work is a useful mechanism to power soft devices able to perform different tasks.¹ In this field, Liquid Crystal Elastomers (LCEs) offer the possibility to convert their molecular rearrangement into a net macroscopic movement, transferring an actuating stimulus into a mechanical work.² Depending on their composition, LCEs are able to change their shape reversibly (thanks to a liquid crystalline to isotropic phase transition)³ in response to all the external stimuli able to induce a LC phase transition (e.g. electric or magnetic fields, temperature, etc.). Their crosslinked structure allows for the initial shape recovery after the removal of such external agents.³ Liquid Crystalline Elastomers have been already investigated for the potential realization of artificial muscles⁴ and for robotic applications using light as the sole energy source, at different length scales.⁵⁻⁷ Moreover, these polymeric networks can be structured in simple layers as well as in complex shapes, from macroscopic films⁸ to microstructures,^{9,10} also opening for their use in different fields, from photonics^{11,12} to biology.¹³

Several studies demonstrate how it is possible to engineering their deformation by modifying the molecular alignment during the synthetic steps.¹⁴ For example, contraction, bending or twisting can be achieved by using the same LCE monomeric formulation and aligning the nematic mixture respectively in a planar homogenous,^{4,8} splayed^{15,16} or twisted way.¹⁷⁻¹⁹

Recently, Selinger et al. demonstrated the out of plane twisting in a chiral smectic LCE film by application of an electric field.²⁰ Similar movements can be generated also in helicoidal structures, obtained for a twisted nematic LCEs that perform a rotation due to the change of the helical handedness under heating.²¹ However, to the best of our knowledge, LCEs performing pure rotation along one axis are not reported in literature.

On the other hand, rotation is a hugely exploited movement in many fields ranging from robotics to telecommunications. In this latter area, rotation can be envisioned as the basic mechanism for beam steering. In optical systems, from huge distances among radars down to the micro scale in optical microcircuits, the use of light as information vehicles requests the need to redirect the signal to different receivers or channels. In fact, this remains a critical phenomenon to address both in fibre-optic connectors,²² free space optical communications,²³ projection displays,²⁴ optical data storage and retrieval (CD-ROM),²⁵ laser guided weapons, etc. Traditional beam steering techniques are based on electromechanical and acousto-optic phenomena. Also non-mechanical beam steering is acquiring more and more attention thanks to the precision steering in addition to small size, reduced weight, and low power consumption. Non-mechanical beam steerers are often based on liquid crystals, even if they do not offer a practical solution for many applications due to their complexity, like for volume holographic step steering,²⁶ or due to the reduced steering angle limitations.^{27,28}

In this article, we present a completely unexplored solution for efficient beam steering over an angle of 360° degrees. By a simple one step fabrication method, we demonstrated LCE fibres that perform different deformations under light activation. Very interestingly, this is the first example of LCE fibres able to rotate under an external stimulus in a complete reversible way. Using such LCE fibre holding a mirror, we

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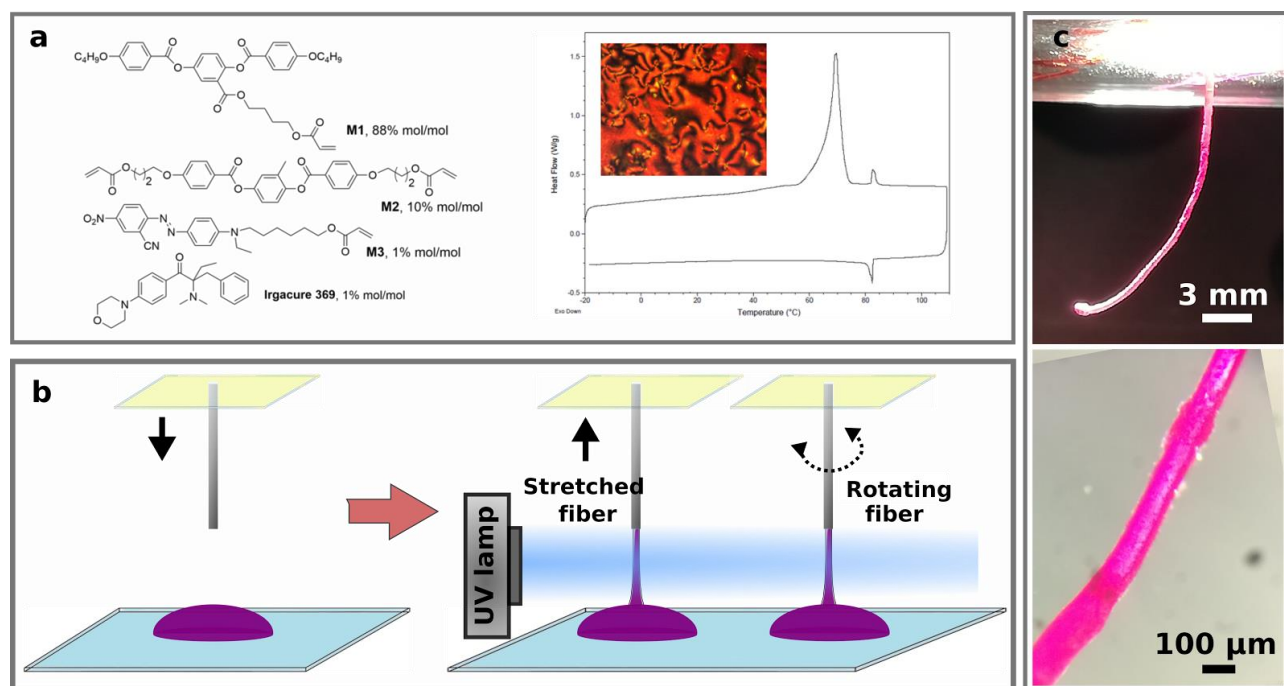


Figure 1. Fibre fabrication. a) Monomer mixture composition (on the left), relative DSC trace (first cycle of heating and cooling, 10°C/min) and POM image at 50 °C on cooling (on the right); b) Scheme of fibre drawn and polymerization; c) Optical images of a rotating and a stretched fibre (top and bottom images, respectively).

demonstrated a light driven beam steerer able to address a laser beam at each direction along a round angle in a controlled manner. In fact, controlling the green laser power, the mirror rotates around the fibre axis and light is deflected at the different angles in a complete fibre turning.

Results and discussion

Liquid Crystalline Elastomer fibres were generally synthesized starting from polymeric precursors that are drawn in the desired shape and then, crosslinked.²⁹⁻³¹ Other techniques to prepare LCE fibres include microfluidic systems³² or electro spray techniques.³³

We developed a LCE fibre preparation method based on simple low molecular weight LC. The LCE mixture, reported in Fig. 1a, is mainly composed by the “side-on” monomer **M1** and the LC crosslinker **M2**. Azobenzene **M3** introduces photoresponsivity to the material⁹ and its absorption spectra does not overlap the UV lamp emission avoiding the azobenzene isomerization during the polymerization process,¹⁶ while **Irgacure 369** promotes UV curing. DSC trace shows at 70 °C the melting of the crystalline mixture into a mesophase that is present up to 82 °C and easily assigned as nematic by POM (Fig. 1a). On cooling, the nematic phase is still present at room temperature and crystallization is not observed by storage of the mixture for several hours. Very interestingly, we combined all the components in order to obtain at room temperature a mixture with a viscosity that allows for the preparation of polymeric wires by mechanical stretching.

In fact, fibre fabrication consists in pulling a thin wire of mixture with a metal bar from a LCE drop as shown in Fig. 1b. A simultaneous UV irradiation leads to fix the fibre shape with the LC alignment retained inside the final material. A different kind of fibre, called here as rotating fibre, is prepared by a similar procedure but combining the stretching of the mixture with a twisting (approximately 10 turns) before the UV irradiation through a motorized rotational stage.

This procedure allows for the preparation of fibres with diameter ranging from 50 to 100 μm and length from 1 to 5 cm (Fig. 1c). No evident differences in the morphology are detected by the observation of the two type of fibres (see Fig. S1). The polymerization is studied by ATR spectroscopy that shows a high degree of conversion after 5 minute of polymerization at room temperature. Acrylate conversion can be further increased by irradiation at higher temperature (Fig. S2).

Mechanical stretching of a nematic liquid crystal is an efficient way to obtain the homogeneous alignment along the shear direction. After removal of the force, the bulk director returns to its initial state. Application of uniaxial shearing was largely employed in different cases, such as the mechanical induction of an isotropic to nematic phase transition in linear polymers,³⁴ or the monodomain alignment in polysiloxane LCE.³⁵ For LCE fibres, the stretching of the material precursor should result in a reversible shortening of the final materials during the nematic to isotropic phase transition.²⁹ To verify the correct LC alignment in our stretched fibres, we first use POM (Figure S4), that shows the transmittance extinction during the fibre rotation, and then we test their shape-changing behaviour. A piece of stretched fibre is suspended in silicone oil and heated up to 140 °C. As shown in Figure 2a, starting from 80 °C the fibre

contracts gradually up to 110 °C. The maximum contraction is the 29% of the original length (Fig. 2a). In accordance, DSC trace of the LCE confirms a nematic to isotropic phase transition with the appearance of an exothermic peak around 100 °C (Fig. S3). The ability to behave as a muscle fibre is translated not only in the material contraction but also in the possibility to hold a certain weight without fibre damage that can be therefore moved following the fibre deformation. A weight is glued to the LCE wire and the fibre is partially irradiated by a green laser (at 85 mW) along 5 mm of its length (diameter of the laser spot size). The irradiation is able to induce the material contraction resulting in the ability to pick up the attached cargo. In this case, only a fibre shortening of 16% is observed (Fig. 2b) due to

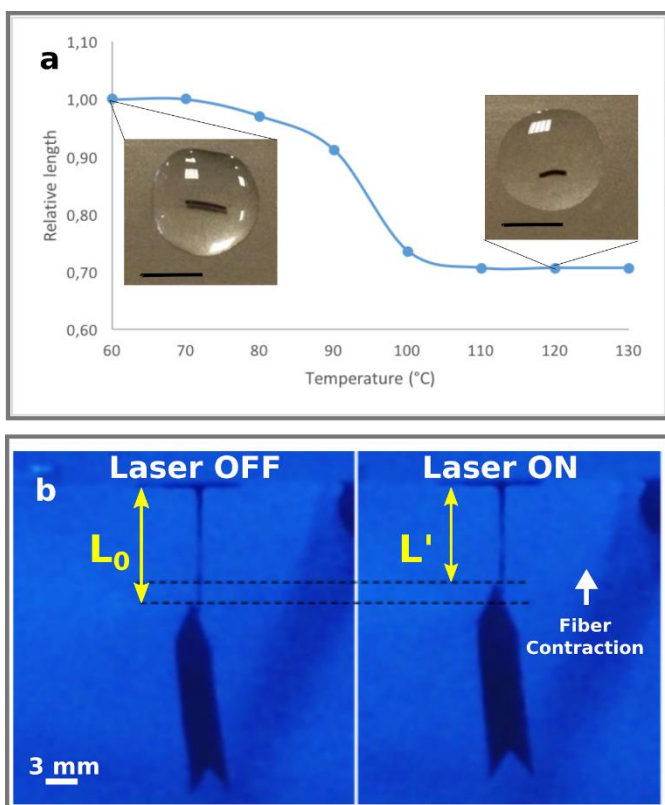


Figure 2. Shape-change behaviour of a stretched fibre. a) Length of a fibre (normalized by the initial length at room temperature) at different temperature and optical images respectively at room temperature and 120 °C (scale bar: 1 cm); b) light induced contraction of a fibre subjected to a cargo (11 mg in respect to the 2 mg weight of the fibre).

combined factors. First of all the irradiation condition. The laser spot covers only a part of the fibre resulting in a lower deformation than those previously reported in Figure 2a. In addition, the fibre contracting force is partially balanced by the weight gravity force. After switching off of the laser, the fibre returns in the original position. Both movements have an evolution dynamics that last in few seconds (1-3 seconds depending on the weight of the attached object), after switching on and off of the actuation laser. The mechanism of deformation in light responsive LCE containing the azobenzene **M3**, as previously reported,¹⁶ is to be attributed mainly to an intermediate heating step, due to the dye absorption and release of heat.

Further tests on the strength of LCE stretched fibres, performed by adding different weights at their ends, show how a fibre of 2 mg is able to efficiently lift objects up to 72 mg in weight (Fig. S5 and Movie S1). The breaking threshold weight is 80 mg, 400 times heavier than the LCE fibre mass.

Rotation of the stretched monomeric mixture leads to a completely different shape-changing behaviour. In fact, such fibres during the phase transition are subjected not only to the contraction but also to a rotation, as depicted in Fig. 3a. Light response of a rotating fibre is completely reported in Movie S2. A paper arrow was attached to the fibre to make evidence of the resulting movement. By switching on the laser irradiation, the arrow rotates performing a complete turn with the same handedness of the rotational shearing applied to the mixture before UV curing. For an activation green laser light of 95 mW,

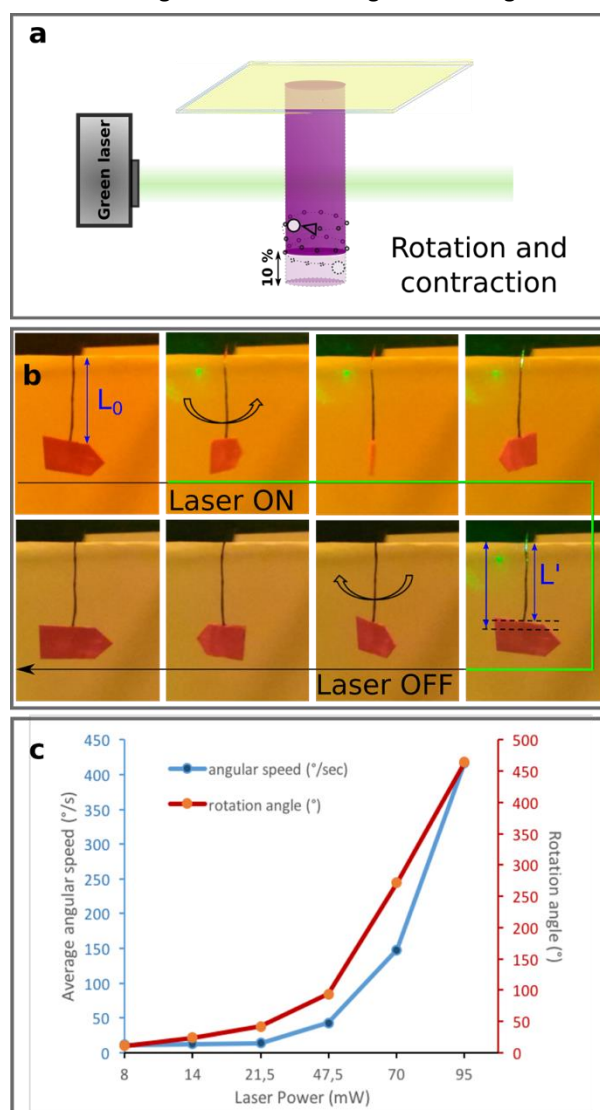


Figure 3. Shape-change behaviour of a rotating fibre. a) scheme of the deformation in a rotating fibre; b) sequence of frames during the irradiation of a fibre with green laser (power= 85 mW) and the return to the original position after switching off the light; c) Angle of rotation of the fibre and relative average angular speed at different power determined for a 1 mg fibre subjected to a 14 mg cargo.

the maximum achieved rotation angle of 450 degrees is obtained in combination with a contraction of around 10% of the fibre. Switching off the laser, rotation in the opposite direction and concomitant expansion occurs, until recovery of the fibre initial position and original length. In Figure 3b, the sequence of frame for the rotation of a 1 mg fibre bearing a 14 mg weight is reported.

The fibre rotation could be the result of a complex alignment inside the monomeric mixture induced by the mechanical shearing applied before the UV curing. In this case, the nematic mixture is subjected to two different mechanical forces. The uniaxial stress is applied by stretching and, as verified in the previous paragraph, a homogeneous alignment is formed. At the same time the mechanical rotation of the mixture would result in the molecule director tilting which follows the rotating shear. The induced alignment can be efficiently frozen by the polymerization. At the end of this process, from the fibre response to green irradiation, we can assume that the molecule director is still parallel to the fibre length, resulting in its shortening, but the non-uniform tilting angle inside the fibre leads to an efficient rotation along the fibre axis.

This new kind of movement together with the possibility to remotely control it, enlarges the application field of LCE. In fact, such rotation can be controlled accurately by using different irradiation powers, which influence both the rotation angle and the average angular speed. The threshold for fibre rotation was found around 8 mW which correspond to a rotation angle of 11°. By increasing the actuating power, both angle and angular speed increase non linearly. Very important, the control of the rotation angle can be achieved by adjusting the laser power.

Once demonstrated the potential of the rotating movement in LCE fibres, we developed a light driven beam steerer with the simple employ of a LCE rotating fibre, a signal can be steered in every 2D direction. This device is constituted by a rotating fibre holding a mirror (a glass cover-slide covered with 30 nm of gold). Fixing the incident direction of the probe laser beam (He-Ne laser with an output power of 5 mW) that impinges on the mirror, we measured the angle of the reflected beam with respect to the incoming light (see Fig. 4a). Controlling the fibre activation power (green laser of 250 mW filtered by a neutral density filter wheel), the reflected beam can be steered along the all 360 degrees (Figure 4b and Movie S3). The power dependence of the steering angle is reported in Figure 4c for the first 180° due to setup limitation but a complete rotation of the fibre has also been achieved (Movie S3).

Also in this case, as the light stimulus is turned off, the mirror recovers the initial position back-reflecting the incident laser. This procedure can be repeated many times (more than 10) and we do not observe any reduction in the maximum rotation. However, the maximum rotation angle is instead influenced by the weight attached to the fibre as highlighted by the comparison of the rotation in the two cases presented here (Fig. 3 and Fig. 4).

The presented beam steerer combines a very simple and cheap fabrication with a remote optical control overcoming typical disadvantages of mechanical and nonmechanical beam

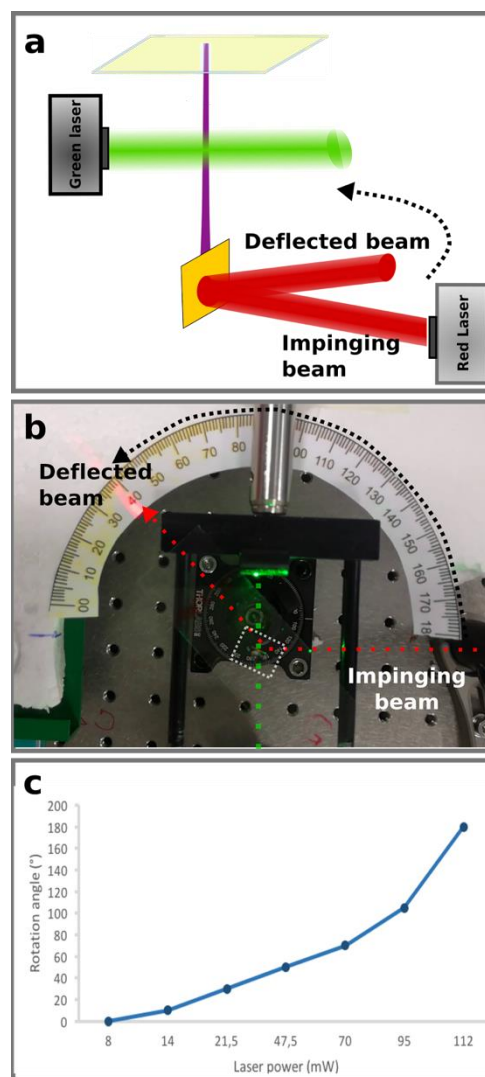


Figure 4. LCE fibre rotation as optically driven beam steerer. a) scheme of the setup; b) example of beam steering by mirror rotation; c) graphic reporting rotation angle at different actuating laser power.

steerers, such as the complexity and the high costs of the former and the reduced steering angle of the latter.

Experimental

General material and methods.

Molecules **M1** and **M3** were prepared as previously reported,^{4,9} **M2** was purchased by Synthron Chemical and Irgacure 369 was purchased from Sigma Aldrich. ATR (attenuated total reflectance) spectra were obtained on a Perkin-Elmer Spectrum 2 instrument. Differential scanning calorimetry (DSC) was carried out using a DSC Q2000 (TA Instruments, Philadelphia, PA) apparatus. Samples of about 3 mg were used and dry nitrogen was used as purge gas. Polarized optical microscopy (POM) was performed using the inverted microscope Zeiss, Axio Observer A1 with cross polarizers.

Fibre fabrication.

Fibres were drawn by mechanical stretching of the liquid crystalline mixture after its melting. In a typical preparation, 5–10 mg of the mixture were placed on a glass and melted on a hot plate at 85 °C. Afterwards, the glass was cooled down until room temperature. The fibres were drawn by dipping the tip of a metal bar and pulling the mixture quickly. Simultaneous irradiation with an UV LED lamp (Thorlabs M385L2-C4, I: 4 mWcm⁻²) for 5 minutes allowed for mixture polymerization and cross-linking. For rotating fibre, the stretched mixture was rotated approximately 10 times before UV curing.

Light induced movement.

Fibres were tested by illumination with a DPSS 532 nm laser from a side. Only a part of the wire was illuminated due to the laser spot (5 mm of diameter) and light intensity was varied using a neutral density wheel-filter. The fibre movement was recorded with a camera (30 fps) equipped with a filter to exclude the excitation wavelength. The indicated laser power values do not correspond to the real activation power because the laser spot of 5 mm diameter exceed the fibre transversal dimension (smaller than 100 µm) and it is thus only partially absorbed, we estimated the absorbed light from the fibres as the 25% of the reported data. Rotation angle and average speed were determined from the movie during the laser irradiation.

Conclusions

Besides the well-known light-driven LCE contraction, we demonstrate how to obtain, in an easy and quick way, fibres which undergo a remotely controlled rotation along one axis. Rotation angle can be controlled by adjusting the power of the actuating stimulus.

We envisaged for such LCE fibres interesting application in photonics. In particular, by holding a mirror on a rotating fibre, we demonstrate the realization of an efficient optically controlled beam steerer. The device combines the advantages from individual gold mirrors, that are highly reflective dispersion-free and polarization invariant, with the realization of large rotation angles, provided by the LCE fibre movement, allowing for deviation of the incoming beam in every in-plane direction of the 360° degrees, only by adjusting the actuating source power. These results open to a new class of beam steerers that will allow to expand LCE applications in telecommunication research fields.

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Notes and references

- 1 F. Ilievski, A. D. Mazzeo, R. F. Shepherd, X. Chen and G. M. Whitesides, *Angew. Chem. Int. Ed.*, 2011, **50**, 1890.
- 2 C. Ohm, M. Brehmer and R. Zentel, *Adv. Mater.*, 2010, **22**, 3366.
- 3 R. S. Kularatne, H. Kim, J. M. Boothby and T. H. Ware, *J. Polym. Sci. Part B: Polym. Phys.*, 2017, **55**, 395.
- 4 D. L. Thomsen, P. Keller, J. Naciri, R. Pink, H. Jeon, D. Shenoy and B. R. Ratna, *Macromolecules*, 2001, **34**, 5868.
- 5 M. Yamada, M. Kondo, J. I. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett and T. Ikeda, *Angew. Chem. Int. Ed.*, 2008, **47**, 4986.
- 6 S. Palagi, A.G. Mark, S.Y. Reigh, K. Melde, T. Qiu, H. Zeng, C. Parmeggiani, D. Martella, A. Sanchez-Castillo, N. Kapernaum, F. Giesselmann, D. S. Wiersma, E. Lauga and P. Fischer *Nat. Mater.*, 2016, **15**, 647.
- 7 H. Zeng, P. Wasylczyk, C. Parmeggiani, D. Martella, M. Burrelli and D.S. Wiersma, *Adv. Mater.*, 2015, **27**, 3883.
- 8 D. Martella, C. Parmeggiani, D. S. Wiersma, M. Piñol, L. Oriol, *J. Mat. Chem. C*, 2015, **3**, 9003.
- 9 H. Zeng, D. Martella, P. Wasylczyk, G. Cerretti, J.C.G. Lavocat, C.H. Ho, C. Parmeggiani and D. S. Wiersma, *Adv. Mater.*, 2014, **26**, 2319.
- 10 S. Nocentini, D. Martella, C. Parmeggiani and D. S. Wiersma, *Materials*, 2016, **9**, 525.
- 11 H. Finkelmann, S. T. Kim, A. Munoz, P. Palffy-Muhoray and B. Taheri, *Adv. Mater.*, 2001, **13**, 1069.
- 12 A. M. Flatae, M. Burrelli, H. Zeng, S. Nocentini, S. Wiegele, C. Parmeggiani, H. Kalt and D. S. Wiersma, *Light Sci. Appl.*, 2015, **4**, e282.
- 13 A. Agrawal, H. Chen, H. Kim, B. Zhu, O. Adetiba, A. Miranda, A. C. Chipara, P.M. Ajayan, J. G. Jacot and R. Verduzco, *ACS Macro Letters*, 2016, **5**, 1386.
- 14 L. T. de Haan, A. P. Schenning and D. J. Broer, *Polymer*, 2014, **55**, 5885.
- 15 G. N. Mol, K. D. Harris, C. W. M. Bastiaansen and D. J. Broer, *Adv. Funct. Mater.*, 2005, **15**, 1155.
- 16 D. Martella, D. Antonioli, S. Nocentini, D. S. Wiersma, G. Galli, M. Laus and C. Parmeggiani, *RSC Adv.*, 2017, **7**, 19940.
- 17 S. Iamsaard, S. J. Aßhoff, B. Matt, T. Kudernac, J. J. Cornelissen, S. P. Fletcher and N. Katsonis, *Nat. Chem.*, 2014, **6**, 229.
- 18 H. Zeng, P. Wasylczyk, G. Cerretti, D. Martella, C. Parmeggiani and D. S. Wiersma, *Appl. Phys. Lett.*, 2015, **106**, 111902.
- 19 J. J. Wie, K. M. Lee, T. H. Ware and T. J. White, *Macromolecules*, 2015, **48**, 1087.
- 20 C. M. Spillmann, J. Naciri, B. R. Ratna, R. L. B. Selinger and J. V. Selinger, *J. Phys. Chem. B*, 2016, **120**, 6368.
- 21 Y. Sawa, F. Ye, K. Urayama, T. Takigawa, V. Gimenez-Pinto, R. L. Selinger, J. V. Selinger, *Proc. Natl. Acad. Sci.*, 2011, **108**, 6364.
- 22 K. Hirabayashi, T. Yamamoto and M. Yamaguchi, *Appl. Opt.*, 1995, **34**, 2571.
- 23 K. Hirabayashi and T. Kurokaw, *Liq. Cryst.*, 1993, **14**, 307.
- 24 D. Faklis and G. M. Morris, *Proc. SPIE*, 1995, **2407**, 57.
- 25 J. J. P. Drolet, E. Chuang, G. Barbastathis and D. Psaltis, *Opt. Lett.*, 1997, **22**, 552.
- 26 H. Kogelnik, *Bell Syst. Tech. J.*, 1969, **48**, 2909.
- 27 H.-C. Jau, Y. Li, C.-C. Li, C.-W. Chen, C.-T. Wang, H. K. Bisoyi, T.-H. Lin, T. J. Bunning and Q. Li, *Adv. Optical Mater.*, 2015, **3**, 166.
- 28 P. F. McManamon, P.J. Bos, M. J. Escuti, J. Heikenfeld, S. Serati, H. Xie and E. A. Watson, *Proc. of the IEEE*, 2009, **97**, 1078.

- 29 J. Naciri, A. Srinivasan, H. Jeon, N. Nikolov, P. Keller and B. R. Ratna, *Macromolecules*, 2003, **36**, 8499.
- 30 T. Yoshino, M. Kondo, J. I. Mamiya, M. Kinoshita, Y. Yu and T. Ikeda, *Adv. Mater.*, 2010, **22**, 1361.
- 31 A. H. Gelebart, M. Mc Bride, A. P. Schenning, C. N. Bowman and D. J. Broer, *Adv. Funct. Mater.*, 2016, **26**, 5322.
- 32 E. K. Fleischmann, F. R. Forst and R. Zentel, *Macromol. Chem. Phys.*, 2014, **215**, 1004.
- 33 S. Krause, R. Dersch, J. H. Wendorff and H. Finkelmann, *Macromol. Rapid Commun.*, 2007, **28**, 2062.
- 34 C. Pujolle-Robic and L. Noirez, *Nature*, 2001, **409**, 167.
- 35 B. Donnio, H. Wermter and H. Finkelmann, *Macromolecules*, 2000, **33**, 7724.