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Thermo-mechanical and photo-luminescence properties of micro-actuators made of liquid crystal elastomers with cyano-oligo(p-phenylene vinylene) crosslinking bridges

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Abstract

Nematic liquid crystal elastomers (LCEs) micropillars with reversible thermomechanical deformations and photo luminescence (PL) intensity variations were successfully fabricated by introducing **a** cyano-oligo(p-phenylene vinylene) dye as chemical crosslinker. The PL intensity of the micropillars decreased and increased reversibly during the thermal-deformation process. We studied in detail the possible factors that influence the PL intensity

variations of the micropillars, including temperature variation, contraction/extension and phase transition. The molecules of the dye mainly kept the “monomer” state in the micropillars during the thermal-deformation process. It was found that the phase transition from nematic to isotropic of the LCEs played the major role in the PL intensity variations. This kind of micropillars may have potential application as fluorescent soft sensors.

1. Introduction

Liquid crystal elastomers (LCEs) are a type of smart materials, which have attracted increasing research interests in recent years owing to their potential applications in smart sensors^[1], high-frequency oscillators^[2, 3], microfluidic device,^[4, 5] gas separation membranes^[6], artificial muscles^[7, 8], and so on. LCEs can be seen as liquid crystalline polymers (LCP) with slightly crosslinked polymer chains, which show both the anisotropic orientation characteristic of liquid crystals and the rubbery elasticity of polymer networks^[9]. The molecular organization in the different phases has a great influence on the properties of the LCEs. In the LC phase, the conformation of the macromolecular backbone is coupled with the orientational order of the mesogen units. For example, in the nematic phase, the orientated mesogens force the polymer chains to stretch along the direction of the orientation^[10-12]. However, when the transition from nematic to isotropic phase takes place, the orientational order is lost; consequently, the polymer chains can go back to the usual random coil conformation. This conformational change induced by nematic to isotropic phase transition causes the macroscopic shape change of LCEs. Meanwhile, thanks to the crosslinked network, the orientational order can be restored to its original state, which endows LCEs with the reversible shape-memory properties. Moreover, the shape variation of LCEs can be produced by using various stimuli, such as light illumination, heating, electric and magnetic fields etc.,

giving the opportunity to develop thermo-responsive^[13-21], photo-responsive^[22-29] and electro-responsive^[30-33] smart LCEs.

Luminescent smart materials responsive to external stimulus, like mechanical stress^[34-36] or temperature^[37], have gained increased attention since they might have applications in sensitive sensors^[38], organic light emitting diodes (OLEDs)^[35] and security printing^[39]. Weder^[40, 41] introduced dye molecules, cyano-p-phenylene vinylene (cyano-OPV) derivatives, as the dopant compound into linear low-density polyethylene (LLDPE) to make stress-sensitive luminescent materials. The tensile deformation of the LLDPE materials forced the cyano-OPV molecules to change from the “excimer” state to the “monomer” state to realize the chromic properties. This kind of deformation-induced fluorescence color change could be used as strain sensors in polymer objects. In a previous study, one of us^[42] mixed similar cyano-OPV molecule (1,4-bis(α -cyano-4-methoxystyryl)benzene) as the dopant with a nematic LCE. Upon the thermomechanical shape change of LCE, they observed, however, only a diminution of the fluorescence intensity during the contraction of the LCE. As a matter of fact, in the systems where shape changes co-exist with temperature variations and phase transitions, other physical phenomena could also affect the PL intensity variations. In particular, the influence of phase transitions **was already reported** in ceramic^[43], gels^[44], and liquid crystal^[45]. G. Meier^[45] et al discovered that the quantum yield of fluorescence of a dye dissolved in a LC mesophase changed dramatically at the phase transition from the nematic to the isotropic phase.

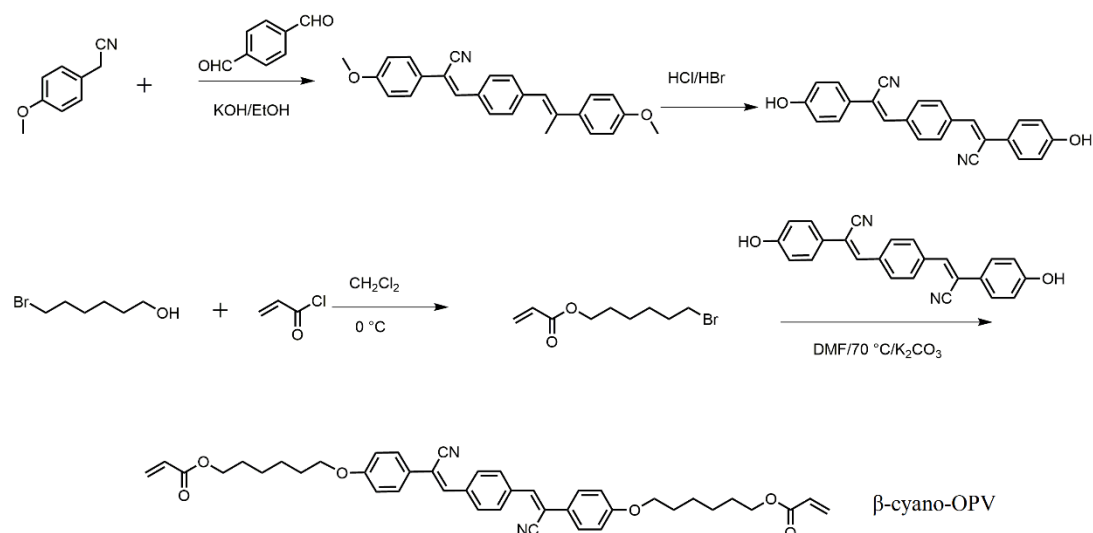
Following this previous work on fluorescent LCEs, we prepared here new nematic LCEs by introducing the fluorescent cyano-OPV dye (**Scheme 1, compound 5**) as the crosslinker which **was thus** connected chemically to the LCEs. The fluorescent nematic LCEs were prepared in the form of micropillars with **different crosslinking degrees and different contents of dye**

crosslinker cyano-OPV in the whole concentration of crosslinkers. Those new micropillars gave us the opportunity to study in detail the relationships between the PL properties and each potential factor influencing the PL intensity, such as temperature change, contraction and extension, and phase transition. The monodomain LCE micropillars were fabricated using β -cyano-OPV ($(((1Z,1'Z)-1,4\text{-phenylenebis(1-cyanoethene-2,1-diyl))bis(4,1\text{-phenylene))bis(oxy))bis(hexane-6,1-diyl) bis(2-methylacrylate)}$), (see Scheme 1) as the dye crosslinker associated with a flexible and non-fluorescent crosslinker and MA444 ((4-methacryloyloxy)butyl 2,5-di-(4'-butyloxybenzoyloxy)benzoate, see Scheme 2) as the nematic monomer, by the previously described magnetic alignment method^[14]. Then the PL intensity variations and the thermomechanical properties of these micropillars were investigated. It was found that the phase transition from nematic to isotropic of the LCEs played the major role in the PL intensity variations.

2. Results and discussion

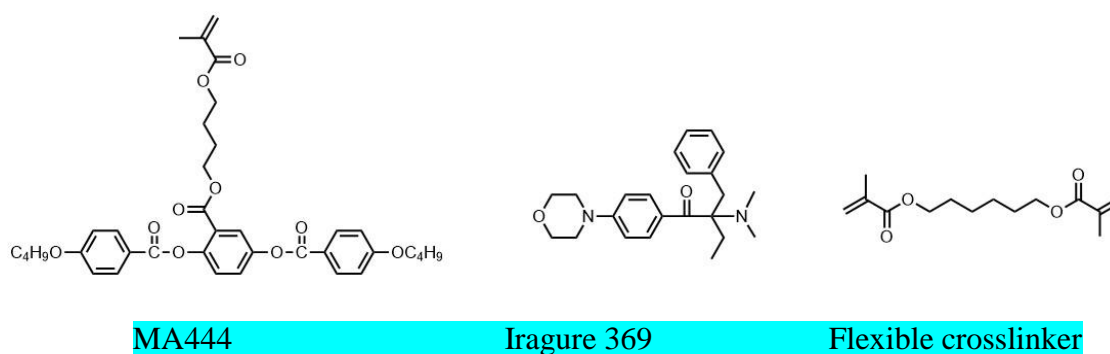
2.1 Synthesis of the dye crosslinker and preparation of LCE micropillars

We first synthesized the dye crosslinker β -cyano-OPV (compound **5**) according to the Scheme 1. The details of the syntheses and characterization are described in the Supporting Information.



Scheme 1. Synthetic route of the dye crosslinker β -cyano-OPV (compound 5).

The phase behavior of the compound **5** was studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The compound **5** exhibits two endothermic transitions at 130°C and 146°C according to DSC measurement (Figure S3 in SI). A complementary analysis by POM helped to identify the phase transition at 130°C as the crystal-to-nematic phase transition, and the one at 146°C as the nematic-to-isotropic phase transition.



Scheme 2. Chemical structures of the monomer MA444, the photo-initiator (Irgacure 369) and the flexible crosslinker.

Then the micron-sized LCE pillars were fabricated by photo-polymerization under magnetic field alignment as previously described ⁽¹⁴⁾, using the mixtures of LC monomer (MA444),

photo-initiator (2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone) and a flexible crosslinker (1,6-hexanediol dimethacrylate) (see Scheme 2) together with the dye crosslinker (compound **5**). The monomer MA444 was synthesized according to the procedure already published. The phase sequence of MA444 are Cr 83 Iso on heating and Iso79 N 60 Cr on cooling^[46]. The concentration of the photoinitiator was kept at 2 mol%, while various concentrations of crosslinkers were used. First on keeping the whole crosslinkers concentration at 10 mol%, the concentration of the compound **5** was varied from 0.5 mol% to 5 mol% in order to study the effect of the dye concentration. Then on keeping the concentration of compound **5** at 1 mol%, LCEs with different whole crosslinker concentrations (10 mol% and 35 mol%) were prepared in order to compare PL properties of slightly and highly crosslinked LCEs. The phase transition of each mixture for micropillar preparation was checked beforehand to ensure that the photo-polymerization occurred in aligned nematic phase.

2.2 Fluorescence properties of the dye crosslinker (compound **5**)

The PL properties of the cyano-OPV derivatives are sensitive to their “environment”, for example in solution or in solid-state (amorphous or crystalline) as reported by Weder et al ^(41, 42). The authors linked this sensitivity to the existence of “monomeric state” versus “excimer state” for the dye molecules when they were “dispersed” versus “aggregated”. Therefore, it is important to characterize the fluorescence properties of the compound **5** in different environments, *i.e.*, in solution, in the LCE micropillars and in pure state.

Figure 1 shows the PL excitation and emission spectra of the compound **5** in different environments. Fluorescence excitation spectra of the compound **5**, both in dichloromethane solution and in the micropillar, are presented in Figure 1a and 1b, respectively. The maximum excitation is around 396 nm in solution, while in the micropillar, the excitation curve

broadens and red-shifts with a maximum around 420 nm. As for the fluorescence emission of the compound **5**, Figure 1c and 1d show very similar emission spectra with maximum around 460 - 490 nm in the CH₂Cl₂ solution and in the micropillars. This observation indicates a similar molecular organization of the dye molecules both in solution and within the elastomer. Since the compound **5** is well dissolved in the dichloromethane, the dye crosslinker is in the monomeric state (unimer) in solution. We can then deduce that the dye crosslinker is also in the monomeric state in the LCE micropillars. Finally, we checked the fluorescence emission of the pure compound **5** in the solid state. As shown in Figure 1e, a sharp emission peak was observed at 515 nm, together with a shoulder emission at 550 nm, which is a typical emission spectrum for the excimer emission as previously ascribed in the literature ^[41]. With naked eyes, we observed that the compound **5** in solid state exhibited a strong green-yellow fluorescence under UV light irradiation (Figure S4). This fluorescence was associated with the presence of excimers as described by Weder et al. ^[41]. The sharp contrast between the emission spectra of the dye crosslinker in pure solid state and in LCE micropillars confirmed again that the dye crosslinker molecules are in the monomeric state both in the LCE micropillars.

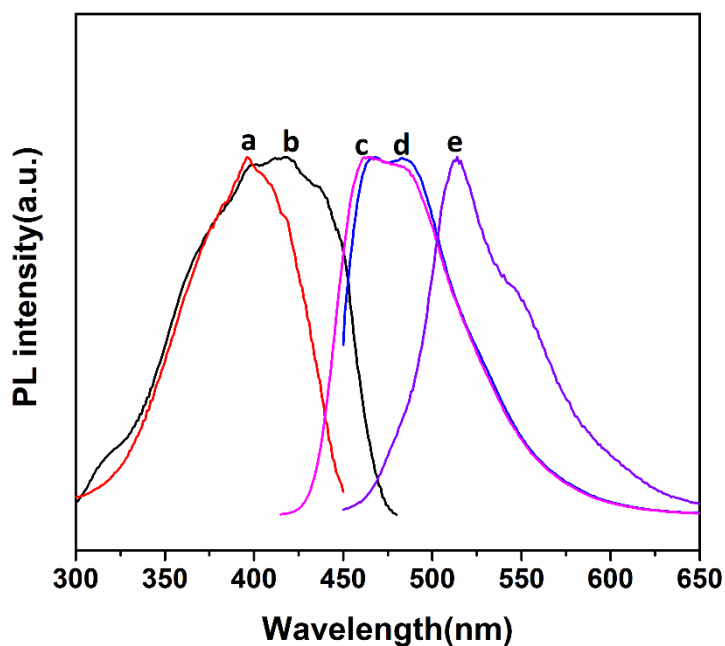


Figure 1. The PL excitation and emission spectra of the compound **5** in different environments. (a) The excitation spectrum in CH_2Cl_2 solution (10^{-5} mol/L). (b) The excitation spectrum in micropillars. (c) The emission spectrum in CH_2Cl_2 solution under the excitation light of 396 nm. (d) The emission spectrum in micropillars under with the excitation light of 420 nm. (e) The emission spectrum in the pure solid state with the excitation light of 420 nm.

2.3 Thermomechanical properties of the LCE micropillars

After the photopolymerization, optical microscopy, scanning electronic microscopy (SEM) and fluorescence microscopy were used to observe the regular array of micropillars and separated micropillars. As shown in Figure 2a, the optical microscopy image showed the regular array of micropillars on a large scale, demonstrating that the method was suitable for preparation of micropillars with a high efficiency and accuracy. SEM image of the micropillars array is presented in Figure 2b, which further confirms the structures. Figures 2c and 2d show the separated micropillars under POM without and with crossed polarizers, respectively. No obvious defects could be observed in the long axis of the micropillars in the Figure 2d, indicative of a relatively good alignment of the nematic mesophase. The regular array of micropillars and the separated micropillars were also observed by fluorescence

microscopy under UV light excitation (365 nm) and blue light excitation (450 nm) as shown in Figure 2e, 2f, 2g and 2h, respectively. The LCE micropillar actuators exhibited a blue emission under UV excitation and a green emission under blue light excitation. The average length of the micropillars was measured to be around 70 micrometers from both the fluorescence images and optical images.

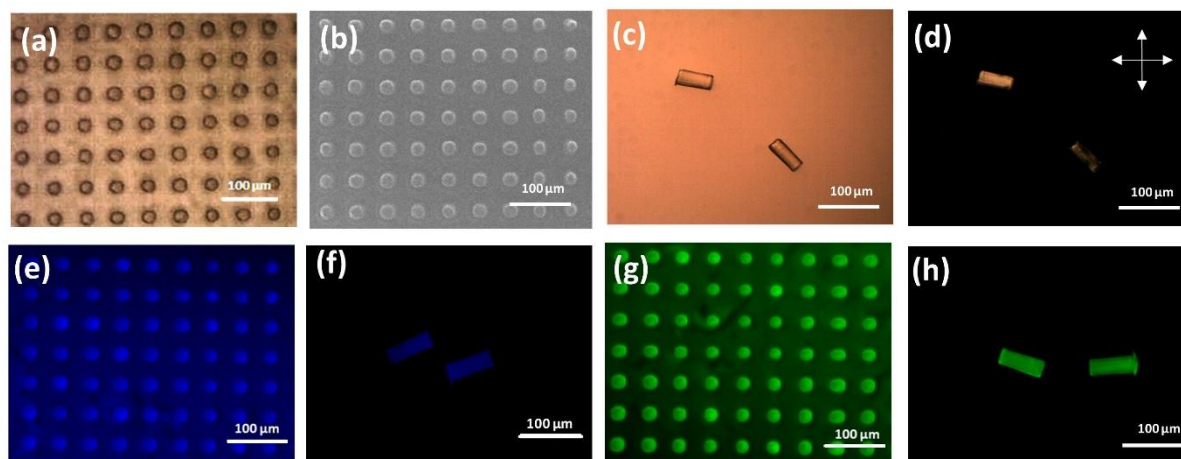


Figure 2. Images of the LCE micropillars containing the β -cyano-OPV as crosslinker. (a): Optical microscopic image of the micropillars. (b): SEM image of the micropillars. (c): Separated micropillars observed under POM without crossed polarizers. (d): Separated micropillars under POM with crossed polarizers. (e) and (f): Fluorescence image of the micropillars excited by UV light of 365 nm. (g) and (h): Fluorescence image of the micropillars excited by blue light of 450 nm.

The thermally-induced actuation properties of the micropillars were investigated by measuring the micropillars lengths at different temperatures. Micropillars were dispersed in a low viscosity silicone oil on a clean glass slide in order to avoid friction between the actuators and the glass surface. The glass slide was kept on a heating stage under the optical microscope. Four different micropillars were prepared with various contents of the dye crosslinker (0.5 mol %, 1 mol %, 2 mol %, 5 mol % respectively) on keeping the whole crosslinkers concentration constant (10 mol%). As an example, the deformation of the micropillars with 1 mol % of dye crosslinker as a function of temperature is presented in Figure 3 (the others are

presented in Figures S5 and S6). Figure 3a shows the thermally-induced spontaneous shape deformation behavior of the micropillars during a heating and cooling cycle between 25 °C and 100 °C. Upon heating at 100 °C, the length of micropillars reduced around 30%. Upon cooling, the length of micropillars recovered to their original value. Then we selected 10 **separated** micropillars to measure their lengths along the longitudinal direction when the temperature was varied from 25 °C to 100 °C and from 100°C back to 25 °C. The contraction and relaxation were characterized by L/L_{iso} as a function of temperature as shown in Figure 3b, where L_{iso} is the minimum length of the micropillar in its isotropic state and L is the length of the micropillar at any given temperature. Contraction during the heating process was observed in the temperature range 70-85 °C, which corresponds to the nematic–isotropic transition temperature (T_{NI}) of the LCE samples (Figure S7). It is clear that the thermomechanical deformation mainly occurs at T_{NI} of the LCEs. On cooling back to 25 °C, pillars expanded and **recovered** the initial shape and size. All these observations demonstrated that the micropillars have a fully reversible shape memory property.

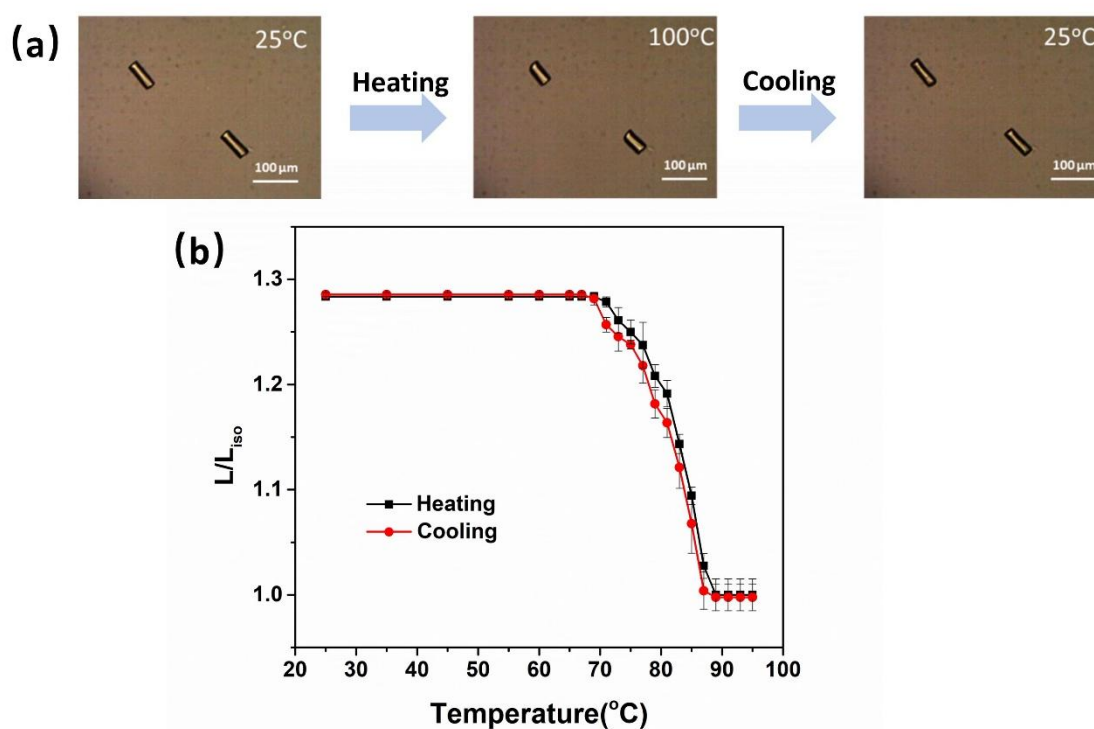


Figure 3. (a) The optical images of micropillars containing 1 mol % dye crosslinker at different temperatures. (b) The contraction and relaxation represented by L/L_{iso} along the long axis of these micropillars at heating and cooling process, 10 micropillars being analyzed. L_{iso} and L are the length of the micropillar in its isotropic state and at any given temperature, respectively.

In addition, the influence of the β -cyano-OPV content on the deformation properties was also investigated. As shown in Figure 4a, the contraction extent L/L_{iso} decreased as the content of the dye crosslinker increased. This observation indicated probably the order parameters of the LC alignment decreased with the increase of β -cyano-OPV content in the crosslinking bridges. Meanwhile, the thermally-induced deformation behavior was repeated ten times to characterized the thermomechanical stability. The contraction and recovery cycling processes were carried out from 25 °C (in nematic phase) to 100 °C (in isotropic phase) and back to 25 °C repeatedly. As shown in Figure 4b, the thermally-induced deformation properties remained stable after 10 successive heating and cooling cycles, which demonstrates the robustness of these micropillars.

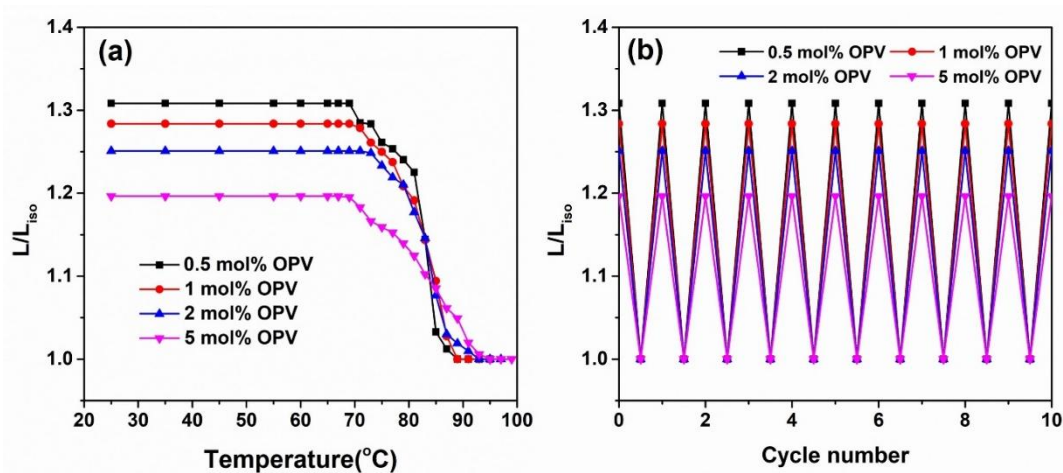


Figure 4. (a) The deformation properties of the micropillars with different concentrations of β -cyano-OPV dye crosslinker. (b) The reversible thermal deformation of these micropillars within 10 heating and cooling cycles between 25 °C and 100 °C.

2.4 Photo-luminescence properties of the LCE micropillars

The fluorescence properties of the micropillars are induced by the fluorescent crosslinker β -cyano- OPV. The PL intensity evolution was studied during the heating and cooling cycle between 25 °C and 105 °C. Two different excitation wavelengths (UV light at 365 nm and blue light at 450 nm) were used for the micropillars in the fluorescence microscope. Under UV excitation, the micropillars emitted blue light, while under blue light excitation, the micropillars emitted green light (Figure 8a and 8d). The fluorescence intensity variations and pillars deformations at different temperatures (25 °C, 105 °C, 25 °C) are presented in Figure 5. When the LCE micropillars were heated to their isotropic phase, the PL intensity decreased, meanwhile the length contracted, as shown in Figure 5b and 5e. After cooling down to 25 °C, the PL intensities of the micropillars recovered to a certain extent.

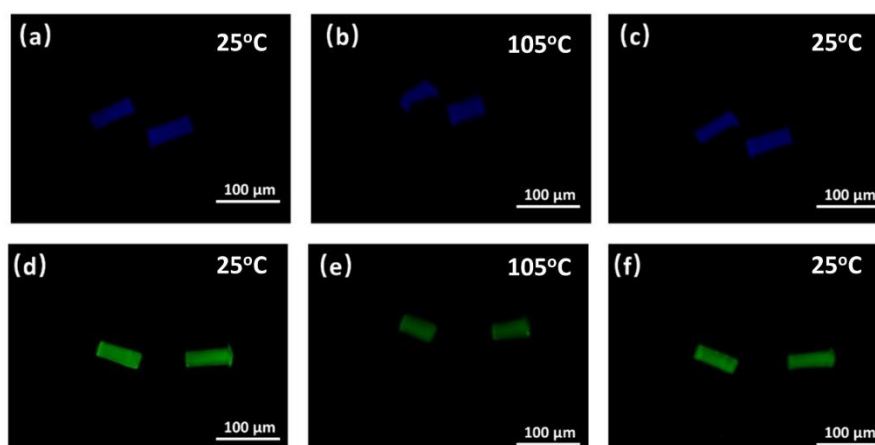


Figure 5. Fluorescence images of LCE micropillars under different excitation lights and at different temperatures. (a), (b) and (c): Fluorescence images at 25 °C, 105 °C and 25 °C under UV light excitation at 365 nm. (d), (e) and (f): Fluorescenc images at 25 °C, 105 °C and 25 °C under blue light excitation at 450 nm.

We then analyzed the variations of the PL intensity and of the length of the micropillars (10 samples) as a function of the temperature with the aid of the ImageJ software, as described in the Experimental Section 4.4. Figure 6 shows the evolution of the PL intensity and the pillar deformation at different temperatures. With temperature increasing, the pillars contracted and

the PL intensity decreased **for both excitation wavelengths**. When the temperature reached 80 - 100°C upon heating, the PL intensity decreased sharply; upon cooling the PL intensity exhibited a fast recovery also within the 100 - 80°C temperature range. These observations indicated that the PL intensity variation was related to the various phenomena occurring within this temperature range: the temperature change, the nematic-to-isotropic phase transition and the deformation of the micropillars. Figure 6 shows the data of the LCE micropillars containing 1 mol% β -cyano-OPV crosslinker. At this stage, we would like to emphasize that the various β -cyano-OPV concentrations used in the preparation of the micropillars did not influence the PL intensity variations (see Figure S8-S13).

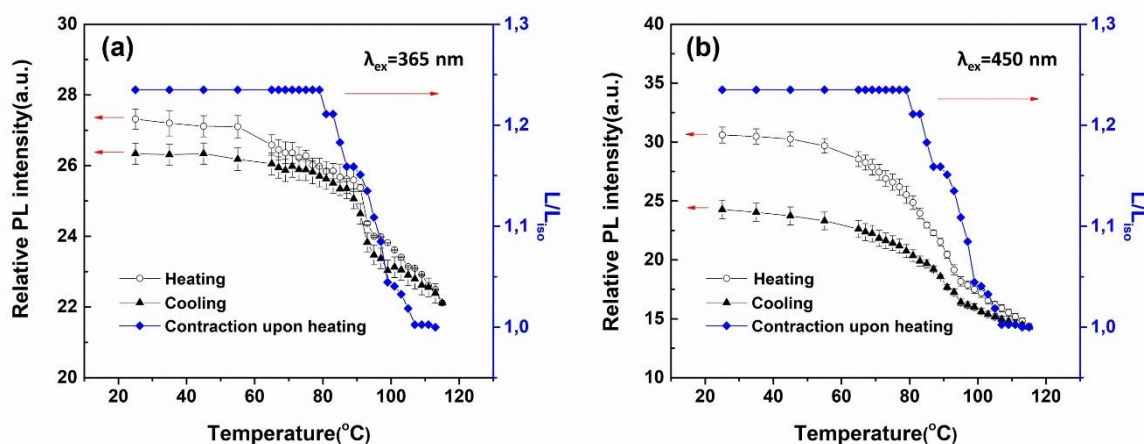


Figure 6. The variation of fluorescence intensity and the ratio of contraction of the micropillars containing 1 mol% β -cyano-OPV crosslinker, as a function of temperature during the heating and cooling process. (a) under UV light excitation at 365 nm. (b) under blue light excitation at 450 nm.

2.5 Analyses of factors that might affect the PL intensity of LCE micropillars

The potential factors which might affect the PL intensity variations during the heating and cooling processes were explored. First of all, during the photopolymerization to prepare the LCE, the β -cyano-OPV dye could also absorb the UV light to **undergo a** photoisomerization.

Therefore, the thermal stability of all the produced isomers in the micropillars may have an effect on the PL intensity. To evaluate the content of possible isomers in the micropillars and their thermal stability, we used the β -cyano-OPV dye in solution in CDCl_3 or DMSO- D_6 (concentration = ?) as model system, which was irradiated during different time until 30 min and then analyzed by $^1\text{H-NMR}$. (Note that 30 min is the duration of photopolymerization). The details are presented in the SI (Section 4). As shown in Table S1 and Figure S15, the study by $^1\text{H NMR}$ spectra indicated that the isomerization took place in β -cyano-OPV in solution after 30 min of UV irradiation. However, after keeping the irradiated β -cyano-OPV solution at room temperature for 30 days in dark or heating up to $110\text{ }^\circ\text{C}$ for 10 min in dark, there was nearly no change in the positions and intensities of the $^1\text{H NMR}$ signals. That means that the isomerized structures are thermally stable. We extrapolated this conclusion to the possible isomers in the LCE micropillars. (We believe this is reasonable because the molecular mobility is lower in LCE than in solution). This indirectly indicated that the possible isomer structures, if they exist in the LCE micropillars, will not be affected during the thermally-induced deformation process. Thus, the observed PL intensity variations do not come from a phenomenon related to a change in the isomerization ratio.

Photo-bleaching is another phenomenon that could induce the decrease of PL intensity. It is related to the photochemical destruction of the fluorophore, which, if present, might also prohibit to perform long observations of our samples by fluorescence microscopy. We have recorded the PL intensities of the micropillars containing 1 mol% β -cyano-OPV at $25\text{ }^\circ\text{C}$ as a function of illumination time until 65 min under UV light (365 nm) and under blue light (450 nm) with the same intensities as those used in other experiments presented in this work. The data presented in Figure 7 show that PL intensity remained stable during more than 1h of illumination. This result suggests that the photo-bleaching can be ignored in our experiments.

Now we discuss one by one the effect on the PL intensities of the three main physical parameters occurring within the temperature range 80 – 100 °C: the temperature change, the nematic-to-isotropic phase transition and the deformation of the micropillars.

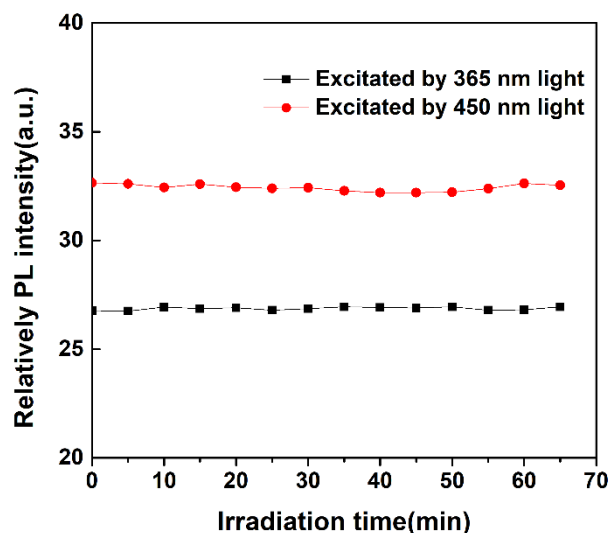


Figure 7. The PL intensity evolution of micropillars containing 1 mol% β -cyano-OPV at 25 °C under the continuous 365 nm UV light and 450 nm blue light illumination.

In order to study the fluorescence sensitivity to a simple temperature variation, we specially fabricated new micropillars containing 1 mol% β -cyano-OPV but a high concentration of whole crosslinkers (35 mol% in total) which was photopolymerized in the isotropic phase. These pillars were not monodomain with aligned mesogens and were densely crosslinked, so that they would not exhibit any thermomechanical effect since they are some kind of polydomain thermosets. The POM of the highly crosslinked micropillars showed a very weak birefringence, as compared to the lightly crosslinked micropillars (Figure S18). Moreover, only one broad peak was observed in the DSC curve (Figure S19), which was ascribed to the glass-to-isotropic phase transition. The PL intensity and the size of these highly crosslinked micropillars were monitored during a heating-cooling cycling process, from 25°C to 115°C. Firstly these micropillars did not change shape and size (Figure S20). Then, as shown in

Figure 8, the PL intensity decrease and recovery during the heating and cooling cycle were smooth without abrupt change with temperature increasing under UV or blue light excitations (more changes were observed under blue light excitation). Thus, a simple effect of temperature cannot explain the sharp PL intensity variation for the LCE micropillars, as reported in Figure 6.

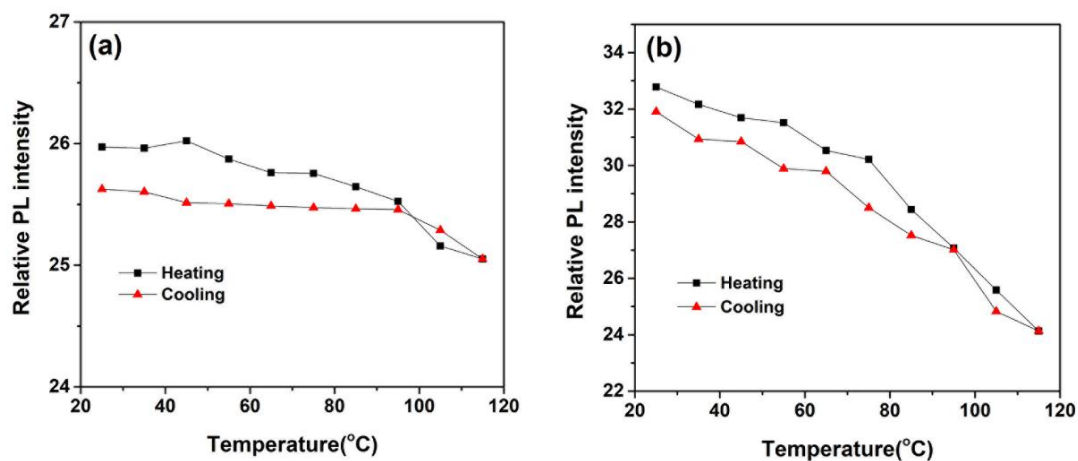
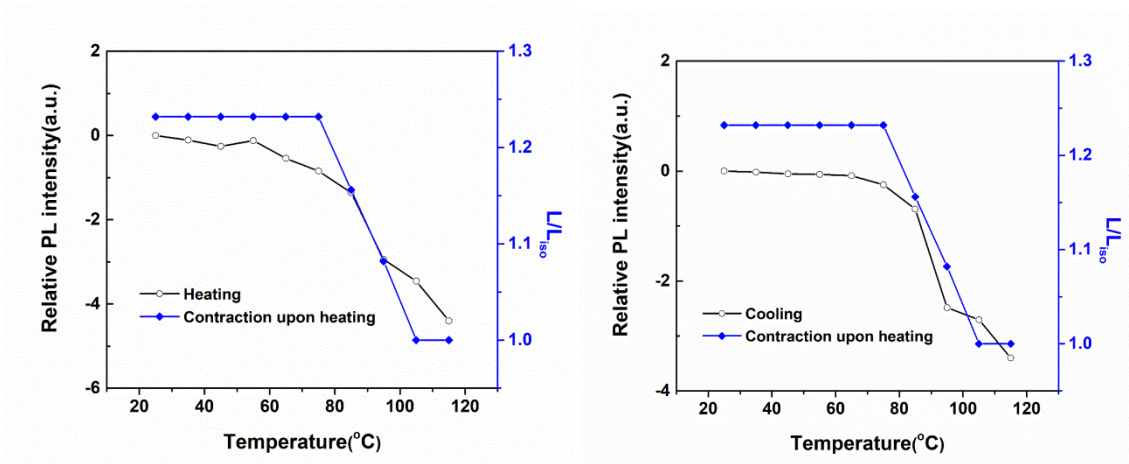
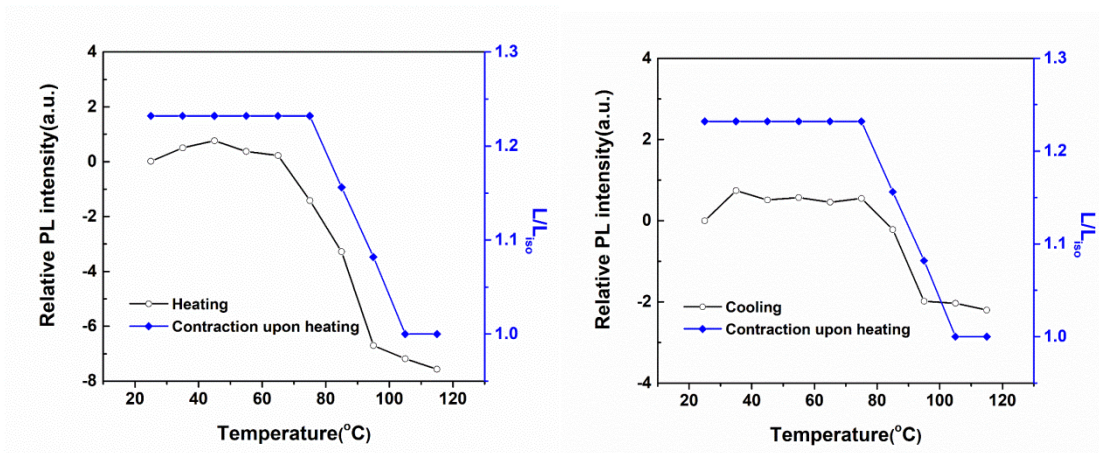


Figure 8. The PL intensity variation with temperature for the highly crosslinked micropillars containing 1 mol% β -cyano-OPV crosslinker under UV light excitations (a) and under blue light excitation (b).

The “natural” decrease of the PL intensity with the temperature can be then deduced from the global variation traced in the Figure 6, leading to the results presented in the Figure 9. The PL intensity variations depend now only on the deformation process and **on** the phase transition.



(a)



(b)

Figure 9. The PL intensity variation after removing the pure temperature effect during the heating and cooling process under the UV light excitation (a) and under the blue light excitation (b).

In order to further study the relative influences of the deformation process and the nematic-to-isotropic phase transition on the PL intensity variation, we built a new experiment. We studied the evolution of the PL intensity as a function of the temperature for an unpolymerized mixture containing the LC monomer, the flexible crosslinker and the β -cyano-OPV crosslinker, but without the photoinitiator. The observed PL intensity variations will

reflect only the evolution connected with the phase transition (nematic-to-isotropic). As shown in the Figure 10a, the PL intensity decreased with the temperature **increase**. In the Figure 10b, the PL intensity variation for the mixture and **the** DSC curve are grouped, demonstrating that the sharp decrease in PL intensity is concomitant with the nematic-to-isotropic phase transition at 70-80°C. We **also** checked out **that** the PL intensity of the pure β -cyano-OPV in **the** solid state was not sensitive to temperature in the studied range (see Figure S21). We could conclude that the PL intensity variation observed for the monomers mixture was caused by the phase transition.

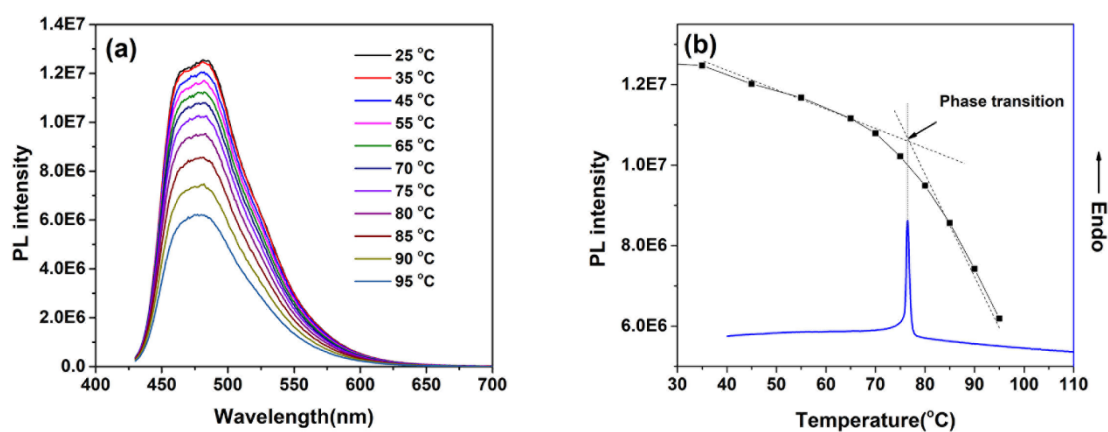


Figure 10. (a) The fluorescence emission spectra evolution with temperature for the LC monomers mixture containing 1 mol % β -cyano-OPV crosslinker under excitation light at the 420 nm. (b) The PL intensity variation at $\lambda_{em} = 481$ nm and the DSC curve of the unpolymerized mixture upon heating.

At last, the evolution of the emission spectra with the concentration of β -cyano-OPV crosslinker in micropillars was investigated. As shown in Figure 11a, when the concentration of the **dye** was 0.5 mol%, the maximum emission spectra had peak value at 476 nm, while for a 5 mol% concentration, the emission peak had a limited red shift to 492 nm. Meanwhile, the variation of the emission spectra with the temperature change was also explored to check the state of the β -cyano-OPV molecules during the deformation process. As seen in Figure 11b, the PL intensity decreased with the temperature increasing. However, the emission spectra did

not show any shift and curve shape change up to the isotropic temperature, which means that the β -cyano-OPV molecules always remained in the “monomer state” during the deformation process. Similar results were obtained for the micropillars with different β -cyano-OPV concentrations (Figure S22). This might be linked with the relative small contraction observed for the LCE micropillars, which prevented the dye molecules to come close enough to each other and build effective aggregates.

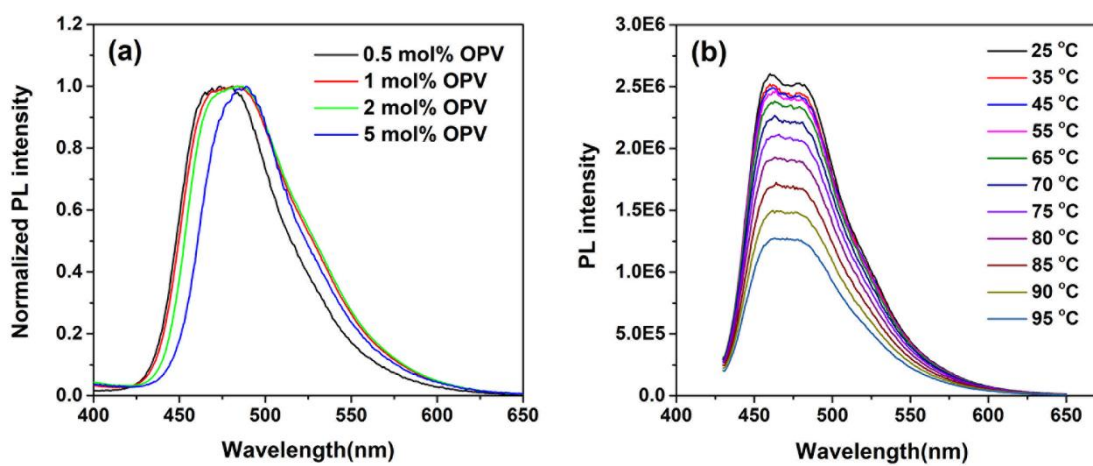


Figure 11. (a) The fluorescence emission spectra of the micropillars with different content of β -cyano-OPV. (b) The thermally-induced PL intensity variation for micropillars containing 1 mol% β -cyano-OPV.

3. Conclusion

We prepared new nematic LCE micropillars by including a fluorescent dye (β -cyano-OPV) as the crosslinker. The potential factors which might affect the photoluminescence intensity during the heating and cooling cycling process were investigated in detail. The nematic-to-isotropic phase transition of the LCE micropillars has the greatest effect on the PL intensity variations. Meanwhile, during the deformation process, no obvious shift of the fluorescence

emission spectra could be detected. We conclude that the β -cyano-OPV dye molecules stayed in the monomeric state during the deformation process of LCE micropillars with the contraction (expansion) ratio L/L_{iso} of 1.25. The study of fluorescent LCEs presenting higher contraction ratio are in progress in order to get excimers and shift of the fluorescence emission spectra. The present work might provide a potential protocol to develop LCE fluorescent sensors and might have potential application in dynamic display device.

4. Experimental Section

4.1. Characterization

^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz spectrometer at 297 K. Deuterated chloroform (CDCl_3) was used as the solvent and TMS (tetramethylsilane) was used as the internal reference.

Calorimetric measurements of elastomers were performed using a Perkin Elmer DSC7 device. The reference cell was kept empty and the sample cell was filled with polymer sample (5 to 10 mg). Samples were scanned over a temperature range between 25 °C and 120 °C with a scanning rate of 10 °C/min.

The fluorescence emission spectroscopy characterization was carried out on a FluoroMax spectrofluorometer. PL dyes samples were dissolved in the dichloromethane (DCM). Fluorescence emission spectroscopy of the LCE micropillars was carried out on the same FluoroMax spectrofluorometer. The LCE micropillars were dispersed in low viscosity silicone oil in a 0.2 cm thickness quartz cell.

UV–Vis spectra were obtained with a PerkinElmer Lambda 800 instrument. The PL dye was dissolved in dichloromethane (DCM) to obtain the spectra in solution.

The PL intensity variations were measured by fluorescence microscopy. Samples were observed directly via a Leica DMIL LED Fluo inverted **microscope** equipped with a Linkam heating stage. The excitation light was supplied by a Cool LED system (pE-300 white, Leica). For the UV light excitation, the fluorescence filter cube of DAPI was used (excitation wavelength between 325-375nm, emission wavelength between 435-485 nm). For the blue light excitation, the fluorescence filter cube of GFP was used (excitation wavelength between 450-490 nm, emission wavelength between 500-550 nm).

Polarizing microscopy (POM) observations were obtained on a Motic BA310POL equipped with a Motic CCD camera, and a Mettler FP 80 hot stage.

4.2. Fabrication of the micropillars

Poly(dimethylsiloxane) (PDMS) molds were prepared via photo-lithography and soft-lithography steps^[47]. **Multiple mixtures were prepared from the monomer MA444 ((4-methacryloyloxy)butyl 2,5-di-(4'-butyloxybenzoyloxy)benzoate), the flexible crosslinker (1,6-hexanediol dimethacrylate) and the β -cyano-OPV crosslinker (((1Z,1'Z)-1,4-phenylenebis(1-cyanoethene-2,1-diyl))bis(4,1-phenylene))bis(oxy))bis(hexane-6,1-diyl) bis(2-methylacrylate)), and the photoinitiator (Iragure 369, (2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone).** The concentration of the photoinitiator was kept at 2 mol%, while various ratios of monomer/flexible-crosslinker/OPV-crosslinker have been tested.

The micron-sized LCE pillars were fabricated as previously described^[14]. The mixture of LC monomer, **flexible and fluorescent crosslinkers**, and photo-initiator were deposited on a glass coverslip placed atop a permanent magnet (~ 1 T NdFeB rare earth magnet) in a heating stage. Then the mixture was heated up to its isotropic phase (100 °C). A soft PDMS mold was gently pressed onto the melted mixture to force the mixture to fill the inner structure of the mold. The monomers mixture was then cooled down to its nematic phase (60 °C) at a slow

rate (1 °C/ min). During the cooling process, the magnetic field aligns the nematic phase with the nematic director pointing along the long axis of the pillars. During the process, an oxygen-free environment was kept by placing the setup in a zip-lock bag flushed with a slow stream of argon. A 365 nm UV light source (30mW/cm²) was used to initiate the photopolymerization for 30 minutes. After the sample was cooled down to room temperature, the PDMS mold was peeled off to leave a regular array of micropillars. A sharp razor blade was used to untie the micropillars from the glass surface. The free micropillars were suspended in low viscosity silicone oil.

4.3. PL intensity measurement of the micropillars

The relative PL intensity variations for the micropillars were measured using Image J software. Keeping the same exposition time (40 ms), gain (2%), Gamma (1) parameters of the fluorescence microscope, the fluorescence images at different temperatures were recorded. The captured fluorescence images were imported in Image J, and changed to an 8-bit grayscale mode. Recording the sum of grayscale values of a fluorescent micropillar in its whole area gave us the relative fluorescence intensity of a micropillar. Ten micropillars were analyzed for each experiment to give the average value.

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