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## Supporting Information

## Smart molecular-spring photonic droplet

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**Figure SI 1**. (a) Preparation procedures for the globally oriented cross-linked CLC film and (b) (i) schematic and (ii) photographic images of the microfluidic chip for CLC-droplet production.



Movie SI 1. Production of the CLC droplets in the microfluidic channel.



Unit = Conc of glycerol (v/v)

(a)



**Figure SI 2**. (a) Photographic images of the droplet in the vials at different contents of glycerol (numbers on the bottom in vol%) in the glycerol/water mixtures and (b) the plot of the contents of glycerol in the glycerol/water mixtures at which the CLC droplet is in the middle of the vial as a function of  $\phi$ .



**Figure SI 3**. Plot of  $\lambda_1$  vs.  $1/\phi$ .



**Figure SI 4.** Optical-microscopy reflection-mode images of the assembled solid-state CLC droplets (made at  $\phi = (i) 20$ , (ii) 24, and (iii) 31 wt%), showing cross-communication patterns. The scale bars represent 20  $\mu$ m.





**Figure SI 5**. (a) UV–vis spectra of (i, —) a dry cross-linked CLC film and cross-linked CLC films in (ii, —) water, (iii, —) methanol, (iv, —) ethanol, (v, —) toluene, and (vi, —) benzene (from left to right in the figure, as indicated by arrow). (b) Photographic bright-field reflection-mode images of cross-linked CLC films (made at  $\phi = 31$  wt%) after dopant extraction in (i) dry state, (ii) water, (iii) methanol, (iv) ethanol, (v) toluene, and (vi) benzene.

**Text SI 1**: For the fabrication of the microfluidic flow-focusing device, PDMS was prepared by mixing the pre-polymer and cross-linker thoroughly at the recommended ratio of 10:1 (w/w). This mixture was degassed for 40 min in a desiccator to remove the remaining air bubbles. The final mixture was poured onto a structured silicon wafer mold, cured inside an oven at 65 °C for 4 h, and removed from the mold. This patterned piece of PDMS was bonded to a pre-cleaned glass microscope slide using a short oxygen plasma treatment (duration of 46 s, Femto Science Inc., South Korea). Figure SI 1b(i) shows a schematic of the microchip, indicating the dimensions of the microfluidic channel. The widths of the inlet channels, orifice, and outlet channel were 40, 40, and 160 µm, respectively, and the depth of the channels was 80 µm throughout. The channel walls and chip assembly were made hydrophilic by treatment with APTES (2 wt% in ethanol) at 20 °C for 10 min and a second treatment at 60 °C for 16 min. The microfluidic chip was mounted under an inverted biological microscope (Samwon NSI-100, South Korea). The liquid samples were supplied to the microfluidic device through flexible plastic tubing (Norton, USA, I.D. 0.51 mm, O.D. 1.52 mm) attached to the reservoir (Fluiwell, Fluigent, France) containing the liquids. The flow rates were controlled using a pneumatic microfluidic flow-rate control system (MFCS-EZ, Flow-Rate Platform and Flow-Rate Control Module, Fluigent) capable of pumping three fluids at a specified velocity. By pumping nitrogen gas into the Fluiwell at a precisely controlled rate, the MFCS-EZ unit was used to pressurize the Fluiwell such that the fluids flowed through the tubes and into the device. The formation of on-chip droplets was imaged using an STC-TC83USB-AS camera (SenTech, Japan) attached to the inverted microscope. The droplets were observed under a polarized optical microscope (ANA-006, Leitz, Germany) with crossed polarizers and a charge-coupled device (CCD) camera (STC-TC83USB, Samwon, South Korea). The dispersed CLC droplets were slowly injected into the middle inlet, and a continuous aqueous phase containing PVA (1 wt%) was injected into the other inlets in a direction perpendicular to that of the dispersed phase. The perpendicular-phase streams met at a junction, and droplet formation occurred when each stream crossed the neck of its channel. The resulting CLC droplets were extracted from the microchip and collected in a  $25 \times 25 \times 3.5$  mm<sup>3</sup> storage reservoir, which was fabricated by gluing a thin silicon rubber sheet onto the glass slide.

**Text SI 2:** We can see from Figure SI 2(b) that the densities of RMM727( $\rho_{RMM}$ ) and CB15 ( $\rho_d$ ) are 1.142 and 1.016 g/cm3, respectively. After UV irradiation, the volume of the mixture was reduced, and the density of RMM727 after UV curing ( $\rho'_{RMM} = \rho_3 = 1.197$  g/cm3) can be calculated using Equation SI (1), where V<sub>2</sub>/V<sub>1</sub> = 0.968 ( $\lambda_2/\lambda_1 = 1/1.033$ ; see the manuscript). The density of the CLC mixture after UV curing ( $\rho_2$ ) can be calculated using Equation SI (2).

$$\rho_{RMM} = \frac{1}{\frac{V_2}{\rho_{RMM}}} - \frac{1}{\frac{V_2}{\rho_d(1-\phi)}} - \frac{\left(1 - \frac{V_2}{V_1}\right)\phi}{\rho_d(1-\phi)} = \frac{1}{\frac{\phi}{\rho_d} + \frac{(1-\phi)}{\rho_{RMM}}} - \frac{1}{\frac{V_2}{\rho_{RMM}}} - \frac{V_2}{V_1} - \frac{V_2}{V_1}$$

**Text SI 3:** A strong and sharp CN stretching band at 2,226 cm<sup>-1</sup> is observed in the spectrum of CB15 (Figure 2a (i)), which is a result of the CN groups at the terminal of the mesogen. The FTIR spectrum of RMM727 before UV curing (Figure 2a (ii)) shows strong –CN and –C=O stretching bands at 2,226 and 1,727 cm<sup>-1</sup>, respectively. The intensity ratio between these bands is 0.09. The FTIR spectrum of the UV-cured CLC film before CB15 extraction (Figure 2a (iii)) shows the same strong –CN and –C=O stretching bands at 2,226 and 1,727 cm<sup>-1</sup>, respectively. Here, the same strong –CN and –C=O stretching bands at 2,226 and 1,727 cm<sup>-1</sup>, respectively. Here, the –C=O band at 1,727 cm<sup>-1</sup> is only a result of RMM727, because no peaks around 1,727 cm<sup>-1</sup> are observed in the FTIR spectrum of CB15 (Figure 2a (i)). The intensity ratio between these peaks is 0.23, which is larger than that for RMM727 (0.09) because the relative amount of –CN groups in the mixture was higher than that for CB15. However, this ratio became 0.08 after the extraction of CB15 (Figure 2a (iv)), which is similar to the ratio for RMM727 (0.09), indicating that CB15 was completely extracted from the CLC film.