

Supporting Information for:

Polymer-stabilized nanoparticle-enriched blue phase liquid crystals

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1. Preparation of the nanoparticles and BPLC mixtures

1.1 Preparation of the nanoparticles

Preparation of ZnS nanoparticles: The hydrophobic surface-treated ZnS NPs with an average diameter of ~33 nm were synthesized in reversed micelle following standard procedures with a slight revision, using Triton X-100 as a surfactant. The preparation was carried out by mixing two reverse micellar solutions with the same water-to-surfactant molar ratio ($W_o = [W]/[S]$) containing the same concentration of Zn^{2+} or thioacetamide. To make a stable reverse micelle, a solution of $ZnAc_2 \cdot 2H_2O$ or thioacetamide was added into a mixture of cyclohexane and Triton X-100, followed by drop wisely adding a small amount of n-butanol as a co-surfactant under stirring. After the mixture became clear, a 1:1 molar ratio of zinc-ion-containing micelle mixed with sulfur-containing micelle, stirred with the aid of ultrasound for the desired time, yields a yellowish emulsion. The XRD spectrum and TEM image of the ZnS NPs have been reported by our previous work,^[1] the ZnS particles have an average diameter of ~33 nm.

Preparation of ferroelectric nanoparticles:^[2,3] The ferroelectric $BaTiO_3$ nanoparticles were prepared by milling large particles (~1 μm in size), which were mixed with a solution of oleic acid (surfactant) in heptane in a weight ratio of 1:2:10, respectively, then the particles were ground in a planetary ball mill for 15 hours. The morphology and particle sizes of the sample were characterized by JEM-100CXII transmission electron microscopy (TEM) operated at 100 kV. A small amount of the powder products was dispersed in heptane and placed in an ultrasonic bath to make a suspension, and then a droplet of the solution was transferred onto a carbon-coated copper grid for the TEM observation. Figure S1 shows TEM image of the $BaTiO_3$ nanoparticles prepared by the above high-energy milling process. As is shown, the $BaTiO_3$ particles have an average diameter of ~30 nm.

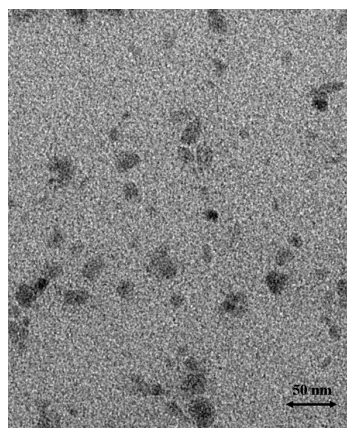


Figure S1. TEM image of the $BaTiO_3$ nanoparticles prepared by a high-energy milling process.

1.2 Preparation of the polymer-stabilized nanoparticle-enriched BPLCs

The BPI-exhibiting LC materials (BPLC) was a mixture comprising the following materials: SLC-X (82.0 wt%, Yongsheng Huatsing Liquid Crystal Co., Ltd, $\Delta n = 0.235$, $\Delta \epsilon = 29.6$ at 298 K), R811 (10.0 wt%, Merck) and Iso-(6OBA)₂ (8.0 wt%, synthesized by our laboratory), and the monomers used in this study to form a polymer network in the composites were Trimethylolpropane Triacrylate (TMPTA, Aldrich) and C6M (Merck). Moreover, the photoinitiator was Irgacure 651 (Aldrich), and the chemical structures of the materials were shown in Figure S2.

The precursors as shown in Table 1 were prepared by dispersing the NPs into the monomers/BPLC composites. In order to achieve good dispersion, the mixtures were dissolved in heptane and sonicated for about 1.0 h. Then, heptane was evaporated off slowly for about 24 h about 45 °C before the samples were placed in a vacuum system at 1023 Torr for 24 h at 50 °C. At last, these precursors were separately heated up to an isotropic phase and then filled into in-plane-switching (IPS) cells with 5 μm electrode width, 5 μm electrode gap, and 10 μm cell gap. Afterwards, UV light ($\lambda \sim 365 \text{ nm}$) with $\sim 2 \text{ mW/cm}^2$ intensity was irradiated for 30 min near the BPI to chiral nematic transition temperature. After UV irradiation, polymer-stabilized nanoparticle-enriched BPLCs were formed. The initial phase assignments and corresponding transition temperatures for the composites were determined by using the thermal optical microscopy with a polarizing microscope (Olympus BX-51), and the temperature was controlled with a hot stage calibrated to an accuracy of $\pm 0.1 \text{ }^\circ\text{C}$ (Linkam LK-600PM).

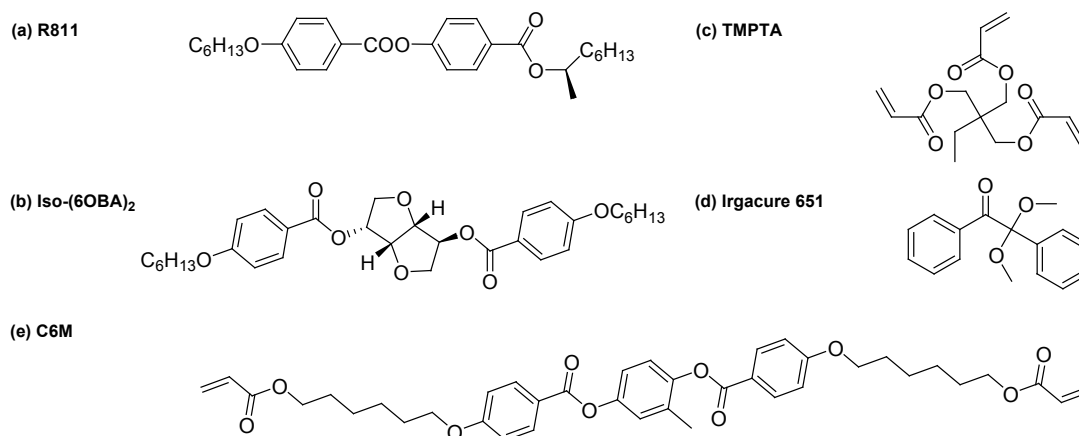


Figure S2. The chemical structures of the materials used.

2. Measurement of the electro-optical performances

2.1 Measurement of electric-induced birefringence^[4,5]

Figure S3 depicts the schematic diagram of the experimental set-up for measuring the birefringence induced by an electric field. The samples in the in-plane-switching (IPS) cells were perpendicularly placed with respect to the incident light. To measure the electric-induced birefringence, an alternating current (AC) rectangular field of 60 Hz supplied by a power amplifier and a function generator was applied between the electrodes in the IPS cell at room temperature. The transmitted light intensity through the cell placed between crossed polarizers was detected by a photodiode. The second harmonic component of the output ac signal from the photodiode was recorded with a digital storage oscilloscope. Herein, the IPS cells were kindly supplied by AU Optronics Corporation, and the indium tin oxide electrode width was 5.0 μm , the distance between the electrodes was 5.0 μm , and the cell gap was maintained at 10.0 μm by spacers.

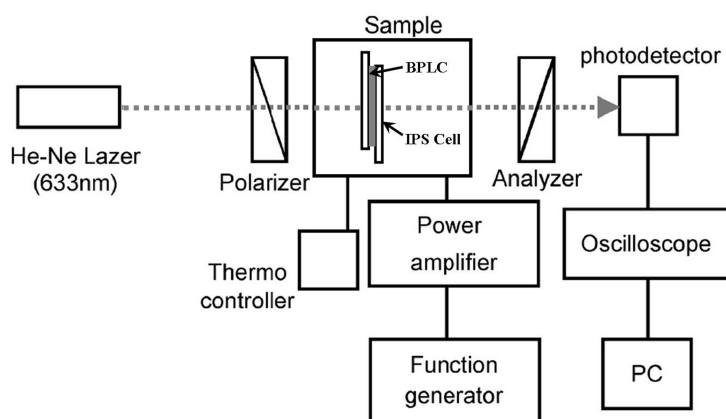


Figure S3. Experimental set up for birefringence measurement.

The change in output intensity due to optical retardation generated by an applied electric field was measured. Output intensity I_{out} is expressed by Eq. (1):

$$I_{\text{out}} = I_{\text{in}} \sin^2(\phi/2) \quad (1)$$

where I_{in} is the input intensity and ϕ is the optical retardation which can be determined by measuring the ratio $I_{\text{out}}/I_{\text{in}}$, correspondingly. The observed change in birefringence Δn is calculated from Eq. (2):

$$\phi = 2\pi\Delta nL/\lambda \quad (2)$$

where L is the length of the light path. i.e., the cell gap between the bottom and top substrates.

Macroscopically, BPLC is an isotropic Kerr medium when there is no external electric field (E) present. As E increases, the BPLC becomes anisotropic along the electric field direction, and the change of the refractive index follows the Kerr effect in the low field region but gradually saturates as the electric field keeps increasing, which can be well explained by an extended Kerr effect. Based on the Kerr effect, the induced birefringence $\Delta n_{\text{induced}}$ in the weak field region is related to E , wavelength λ , and Kerr constant K as:

$$\Delta n_{\text{induced}} = \lambda K E^2 \quad (3)$$

2.2 Calculation of the Kerr constant K ^[5,6]

Based on the data from the measurement of electric-induced birefringence, we can get the plot for the electric birefringence of BPLC a function of the square of the applied electric field, and the electric birefringence is approximately proportional to the square of the electric field, i.e., the equation for the Kerr law Eq. (3) is followed and the slope indicates the Kerr constant. Figure S4 illustrates the variation of induced birefringence with square of an applied electric field in the PSBP doped with 0.5 wt% ZnS nanoparticles (B3) at room temperature. From the slope, we can get the Kerr constant: $\sim 7.75 \times 10^{-10} \text{ mV}^{-2}$.

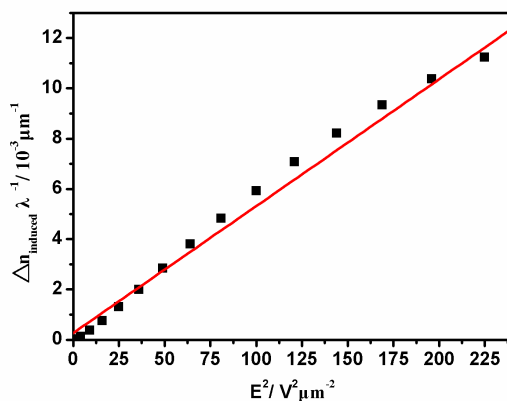


Figure S4. Variation of induced birefringence with square of an applied electric field for PSBP doped with 0.5 wt% ZnS nanoparticles at room temperature.

3. Response times of the polymer-stabilized nanoparticle-enriched BPLCs

The response time for the rise process is defined as t_{0-90} (t_{on}), which is the time for the increase in the transmittance from the initial state to 90% of the saturated state. That for the decay process is defined as t_{100-10} (t_{off}), which is the time for the decrease in the transmittance from the initial state to 10% of the saturated state. Table S1 shows the response time (t_{on} , t_{off}) for the PSBP doped with different concentration of ZnS or BaTiO₃ at room temperature (Sample B1~B5 and Sample C1~C5 as shown in Table 1).

Table S1. The response time (t_{on} , t_{off}) for the PSBP doped with different concentration of ZnS or BaTiO₃ at room temperature.

Nanoparticles	Response Time / ms	Concentration of Nanoparticles / wt%						
		0	0.1	0.3	0.5	0.7	1.0	1.5
ZnS	t_{on}	0.52	0.53	0.54	0.54	0.55	0.59	0.62
	t_{off}	0.49	0.48	0.48	0.46	0.42	0.40	0.53
BaTiO ₃	t_{on}	0.52	0.49	0.47	0.45	0.42	0.51	0.52
	t_{off}	0.49	0.48	0.45	0.40	0.40	0.44	0.47

4. Electro-optical performances of the pure PSBP

Figure S5 shows the voltage-transmittance curve of the pure PSBP (Samples A1~A5) with different concentrations of monomers as a function of applied AC rectangular voltage of 60 Hz at room temperature. The weight ratio of the di-functional monomer to tri-functional monomer was fixed at 5/4, and the overall monomer concentrations were controlled ranging from 3.0 wt% to 15.0 wt%. The on-state voltage (V_{on}), corresponding to the voltage of peak transmittance, increases with increasing the concentration of the monomers, and the samples with 3.0 and 5.0 wt% monomers have the V_{on} of less than 100.0 V but serious hysteresis is observed. Moreover, the hysteresis is relatively small and can be considered as hysteresis free in the samples stabilized by more than 9.0 wt% monomers, but the V_{on} is so high (> 110.0 V).

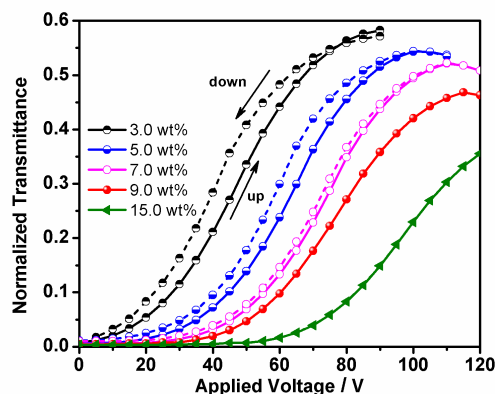


Figure S5. Voltage-transmittance curve of the pure PSBP with different concentration of monomers as a function of applied AC rectangular voltage of 60 Hz at room temperature.

5. The physical parameters of host nematic LCs

The physical parameters of host nematic LCs doped with different concentrations of ZnS or BaTiO₃ NPs, which have been checked at 298K, are summarized in **Table S2**.

Table S2. Observed physical parameters of host nematic LC dispersed by ZnS or BaTiO₃ NPs at 298 K.

SLC-X/ wt%	Nanoparticles / wt%	ZnS		BaTiO ₃	
		Δn	$\Delta \epsilon$	Δn	$\Delta \epsilon$
100.0	0.0	0.235	29.6	0.235	29.6
99.9	0.1	0.235	29.9	0.235	30.5
99.7	0.3	0.237	30.1	0.240	32.1
99.5	0.5	0.236	30.7	0.237	35.9
99.3	0.7	0.238	31.8	0.243	38.3
99.0	1.0	0.237	33.9	0.248	41.7
98.5	1.5	0.239	35.6	0.251	45.2

References for Supporting Information

- [1] L. Wang, C. Zhao, F. Meng, S. Huang, X. Yuan, X. Xu, Z. Yang and H. Yang, *Colloids and surfaces A: Physicochem. Eng. Aspects* **2010**, *360*, 205.
- [2] H. Atkuri, G. Cook, D. R. Evans, C. I. Cheon, A. Glushchenko, V. Reshetnyak, Y. Reznikov, J. L. West and K Zhang, *J. Opt. A: Pure Appl. Opt.* **2009**, *11*, 024006.
- [3] A. Schurian and K. Barner, *Ferroelectr. Lett. Sect.* **1996**, *20*, 169.
- [4] L. M. Sabirov and D. I. Semenov, *Opt. Spectrosc.* **2006**, *101*, 299.
- [5] Y. Haseba and H. Kikuchi, *J. Soc. Info. Display* **2006**, *14*, 551.
- [6] M. Lee, S. T. Hur, H. Higuchi, K. Song, S. W. Choi and H. Kikuchi, *J. Mater. Chem.* **2010**, *20*, 5813.