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Chiral-induced self-assembly sphere phase liquid crystal with fast switching time

Ji-Liang Zhu,[1] Shui-Bin Ni,[1] Chao Ping Chen,[1] Dong-Qing Wu,[2] Xiao-Long Song,[3]
Chao-Yuan Chen,[3] Jian-Gang Lu,[1,a)] Yikai Su,[1] and Han-Ping D. Shieh[1,4]
[1]*National Engineering Lab for TFT-LCD Materials and Technologies, Department of Electronic Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*
[2]*College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*
[3]*The Jiangsu Hecheng Display Technology Co., Ltd., Nanjing 211300, China*
[4]*Department of Photonics and Display Institute, National Chiao Tung University, Hsinchu 300, Taiwan*

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A fluid self-assembly sphere phase (SP) of liquid crystal induced by chiral dopant is observed in a narrow temperature range between isotropic and blue phase or between isotropic and chiral nematic phase. The SP consists of three-dimensional twist spheres (3-DTSs) and disclinations among 3-DTSs. The temperature range of the SP has been broadened to more than 85 °C by stabilizing the disclinations with amorphous polymer chains. The electro-optical switching time of the polymer-stabilized SP is demonstrated in sub-millisecond with a low switching electric field of 4.4 V μm^{-1}, which is of promising applications in displays, 3-D tunable photonic crystals, and phase modulators. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4867358]

The polymer films comprising of liquid crystal droplets dispersed in a matrix have attracted much interest for their potential applications in displays, phase modulators, and three-dimensional (3-D) tunable photonic crystals.[1–4] As a typical example, polymer dispersed liquid crystal (PDLC)[5] can be switched between scattering and transparent states by applying an external electric field. With relatively low concentration of monomers, the PDLC device can be driven with a low switching electric field and shows a slow switching time (>5 ms) owing to the large size of liquid crystal droplets. With relatively high concentration of monomers, nano-scale holographic (H) PDLCs droplets are formed, resulting in fast switching time, usually of less than 1 ms.[6–9] Nonetheless, to reorient liquid crystal molecules in these small droplets, a high switching electric field (15–20 V μm^{-1}) is required for the large anchoring energy of polymer. Many efforts have been made to reduce the switching electric field of HPDLC.[10–13] For instance, the switching electric field can be significantly decreased by using partially fluorinated monomers, conductive particles, or a small portion of surfactants, but they are inevitable to lead to other issues, such as slow response time, poor stability, or low electric resistance. With current PDLC materials, it is difficult to achieve low switching electric field, fast response time, and high stability, simultaneously.

To reduce the size of liquid crystal droplets, chiral doping was introduced to form different chiral system because of the self-assembly of liquid crystal molecules induced by the chiral doping,[14,15] such as chiral nematic phase (N*),[16,17] chiral smectic phase,[18] twisted grain boundary phase,[19] and blue phases (BPs).[20–23] The configuration of the chiral system depends on the elastic constant of liquid crystal host and the proportion of chiral dopant in the system. By introducing sufficient amount of chiral doping into a liquid crystal host, the liquid crystal host with large elastic constant is more conducive to induce the double twist cylinder (DTC) structures of blue phase, rather than the simple twist structure of the N*.[24,25] The switching time of BP, usually of less than 1 ms, is much faster than that of the N* due to its nano-scale chiral pitch.[26] Meanwhile, since these chiral systems do not have any polymer, the switching electric field is lower than that of the HPDLC. Herein, compared with the DTC, a nano-scale three-dimensional twist sphere (3-DTS) can be achieved by the material systems with chiral dopant and liquid crystal materials of larger elastic constant.

In this work, we demonstrate a phase of liquid crystal consisting of highly fluid self-organized of liquid crystal molecules 3-DTSs induced by chiral dopant, which is termed as sphere phase (SP). Sphere phase is usually observed in a narrow temperature range between isotropic phase (Iso) and N* due to its weak thermal stability of the disclination among the 3-DTSs. By introducing polymer system, the temperature range of sphere phase can be broadened to more than 85 °C by stabilizing the disclinations with amorphous polymer chains. Because of the nano-scale chiral pitch and small anchoring energy, the polymer-stabilized (PS) sphere phase can be switched between scattering and transparent states with a switching time of 10^{-4} s and a low external electric field of 4.4 V μm^{-1} at room temperature.

In order to form the 3-DTSs, the nematic liquid crystal material with a large elastic constant is needed. To obtain a large elastic constant nematic liquid crystal material, 20 wt. % rod-like molecule (RLM) 1(3,4-difluoro-4′-(4′-pentyl[1,1′-bicyclohexyl]-4-yl)-1,1′-Biphenyl) was mixed in 80 wt. % nematic liquid crystal host (HC-1015X, HCCH). For comparison, we also prepared another mixture consisting of 80 wt. % HC-1015X and 20 wt. % RLM 2 (1,2-difluoro-4-[(trans,trans)-4′-pentyl[1,1′-bicyclohexyl]-4-yl]-Benzene). Figures 1(a) and 1(b) show the chemical structure of RLM 1 and RLM 2. Compared with RLM 2, RLM 1 has a biphenyl group, which is conducive to increase the elastic constant of the liquid crystal mixtures, as shown in Fig. 1(c). To induce

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[a)] Electronic mail: lujg@sjtu.edu.cn

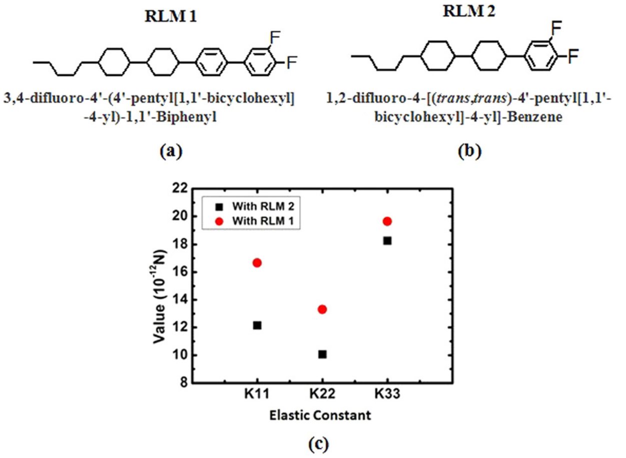

FIG. 1. (a) Chemical structure of RLM1, (b) chemical structure of RLM2, and (c) the elastic constant of the mixtures with RLM 1and with RLM 2.

self-assembly of liquid crystal molecules, a chiral dopant (R1011, HCCH) was added into the mixtures. These homogeneous mixtures were filled into sandwiched cells comprising of two indium-tin-oxide (ITO) glass substrates without alignment layer at an isotropic phase. The temperature of the cell was precisely controlled by a temperature controller (HCS302, Instec Co.) The phase sequence of the mixtures was observed by a polarized optical microscope (POM, XPL-30TF).

Phase transition of the mixture consisting of 69.2 wt. % HC-1015X, 17.3 wt. % RLM 1, and 13.5 wt. % R1011 was investigated, as shown in Fig. 2. From 67 °C to 47 °C, the mixture showed the following phase sequence: Iso 64.1 °C SP, 59 °C SP & BP, 58.4 °C BP, 53.1 °C N*, where sphere phase is observed between Iso and BP at the cooling rate of 0.1 °C /min. During the cooling process, sphere phase appeared between 64.1 °C and 59 °C, which can be identified by the phenomenon of light scattering (Fig. 2(b)). During cooling from 59 °C to 58.4 °C, the coexistence of sphere phase and BP was observed, as shown in Fig. 2(c). The concomitant of sphere phase and BP revealed that 3-DTS and DTC can coexist and they have the same magnitude of helical pitch of nano-scale. To confirm the stable existence of SP, the cell was maintained at 61 °C for over two weeks with the same texture, as shown in Fig. 2(b). The classical platelet texture of BP appeared between 58.4 °C and 53.1 °C (Fig. 2(d)). As shown in Fig. 2(e), the chiral nematic phase appeared below 53.1 °C.

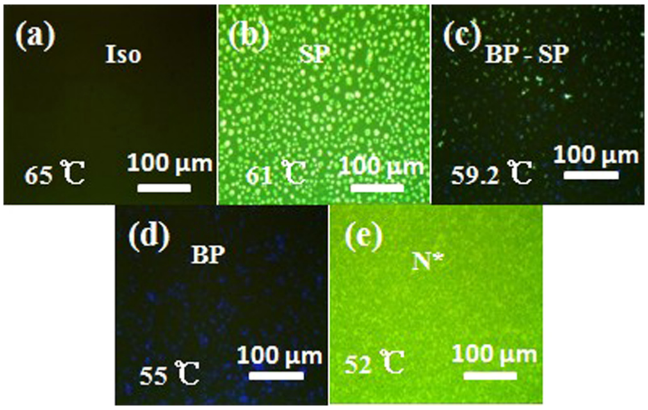

FIG. 2. Polarizing microscopic photographs in phase transition from isotropic phase (Iso) to chiral nematic phase (N*). (a) The sample with RLM 1: (a) Iso, (b) SP, (c) SP-BP, (d) BP, and (e) N*.

The phase transition of the mixture consisting of 69.2 wt. % HC-1015X, 17.3 wt. % RLM 2, and 13.5 wt. % R1011 was investigated. Though RLM 1 and RLM 2 show similar chemical structure, the sphere phase did not appear in the mixture with RLM 2 with any weight concentration of R1011.

To analyze the structure of sphere phase, we then inspect the pattern of sphere phase by changing the angle between the polarizer and analyzer (θ), as shown in Fig. 3(a). The central part of sphere phase texture is bright when θ is 90°. When θ changes from 90° to 0°, the central part of sphere phase texture gradually turns to dark. Therefore, the sphere phase has optical rotation due to the spatial twist of liquid crystal molecules.[12] For these optical properties, the sphere phase may be considered to consist of 3-DTS structures. As depicted in Fig. 3(b), the molecules in 3-DTS structure show double twist in the plane which is perpendicular to the z axis. On the outermost circumference of the double twist structure including the origin of z axis, the molecules are twisted by 45°, with respect to the z axis, from -45° at one end to $+45^\circ$ at the other. As the distance from origin increases in z axis, the size of double twist structure decreases. The director lines of liquid crystal molecules are thus twisted and join two point defects at the poles of 3-DTS, thus the disclinations are formed. Therefore, the sphere phase is formed by the coexistence of 3-DTSs and disclination among 3-DTSs. Schematic illustrations of the proposed arrangement of 3-DTSs in sphere phase and the corresponding arrangement of disclination are shown in Figs. 4(a) and 4(b), respectively. Due to its sphere

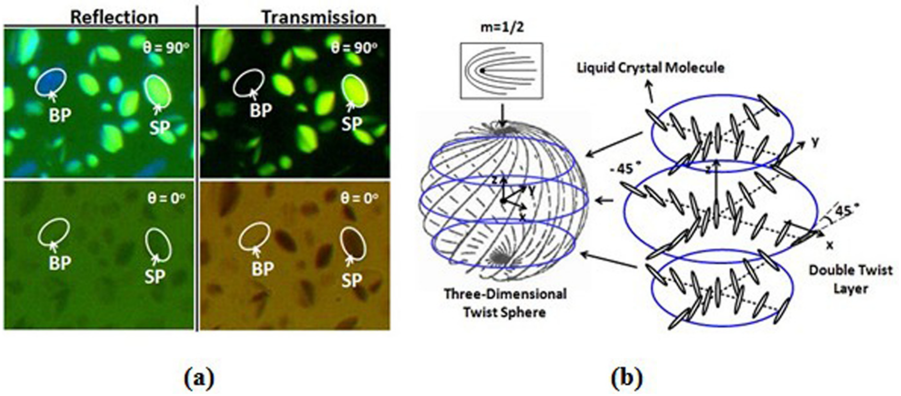

FIG. 3. (a) Polarizing microscopic photographs of SP & BP HC-1015×: R1011/86.5:13.5) with $\theta = 90^\circ$ and $\theta = 0^\circ$ and (b) a model of 3-DTSs in sphere phase.

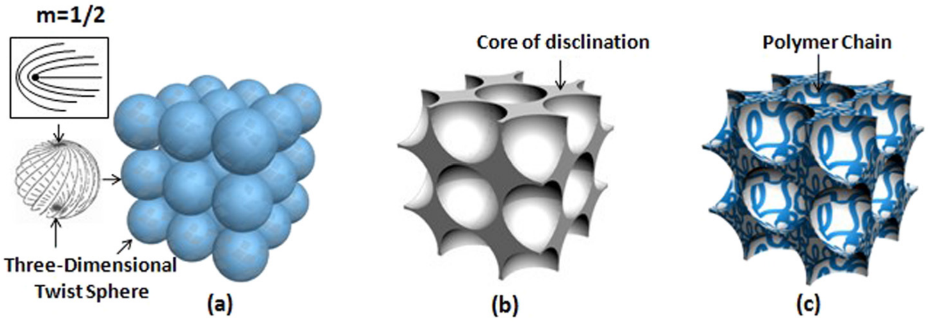

FIG. 4. A model of sphere phase, (a) arrangement of 3-DTSs, (b) corresponding disclination, and (c) an aggregation state of polymer chains in a polymer-stabilized sphere phase liquid crystal.

structure, it is termed as sphere phase. The disclinations are assumed to be isotropic liquid.

The free energy of disclination core F for a sphere phase is expressed by Eq. (1) (Refs. 27 and 28)

$$F = W(T, \sigma, R) - W(K, m, R), \tag{1}$$

where T is a temperature near the phase transition temperature (T_{Iso}) between the sphere phase and Iso, σ is the surface tension of the disclination core, R is radius of the disclination core, K is the Oseen-Frank elastic constant concerning the splay, twist, and bend distortions of the director, m is the strength of topologically disclination core, and defined as the ratio $m = \alpha/2\pi$, where α is the angle by which the director rotates after the traversal of the Burgers circuit surrounding the core. The first term in Eq. (1) represents the energy including excess free energy of the disclination core below T_{Iso} and an interfacial energy between the disclination core and the external chiral material. The second term, which makes F below zero, is elastic energy of disclination cores.

In the model of an isotropic core, the elastic energy of disclination cores, W, is given by Eq. (2) (Ref. 29)

$$W = \pi K m^2 \left(\ln \frac{R}{r_c} + 1 \right), \tag{2}$$

where r_c is cut-off radius of the disclination core. Figure 4(a) depicts the strength of the disclination core in sphere phase, $m = 1/2$, which is the same constant as the strength of disclination core among the DTCs in BP. The sphere phase exists between Iso and BP. Therefore, the free energy of disclination cores in sphere phase is lower than that in BP. To lower the free energy of disclination cores in sphere phase, the elastic constant of the chiral system should be larger than that of the blue phase liquid crystal (BPLC) materials.

The thermal stability of the sphere phase, similar to the BP, is very weak due to its disclinations. Hence, it is usually observed in a narrow temperature range, usually of less than several °C. Based on the principle of polymer-stabilized BPLC,[30] we attempt to broaden the temperature range of sphere phase by using polymer network and this material is termed as PS-SPLC. In the precursor, 8 wt. % of photocurable monomers [4 wt. % RM257 (HCCH) + 4 wt. % 12 A (HCCH)] and 0.3 wt. % of photoinitiator were added into the 91.7 wt. % of the mixture (HC-1015X: R1011/86.5:13.5). Then the precursor was filled into an empty cell with 4.5 μm cell gap, whose inner surfaces were coated with thin ITO electrode at Iso. The cell was cooled down to sphere phase (25 °C) and then cured under a UV light ($\lambda = 365$ nm) with an intensity of 3 mW/cm^2 for 10 min. After polymerization, the sphere phase was observed from 65 °C to −20 °C.

Polymer is more miscible at an Iso than other liquid crystal phases since the miscibility of polymer with liquid crystal depends on the degree of orientational order of the liquid crystal molecules. Therefore, it is reasonable to assume that the polymer chains are selectively concentrated in the disclination which is of isotropic, rather than in the 3-DTS. A possible model structure is illustrated in Fig. 4(c). The polymer chains localized in the disclination in a random coil conformation will keep the orientational order of the liquid crystal molecules at an isotropic state, resulting in a wide temperature range of sphere phase.

The electric-optic property of PS-SPLC was investigated. The PS-SPLC can be switched between scattering (Fig. 5(a)) and transparent states (Fig. 5(b)). The switching electric field of the PS-SPLC, 4.4 V μm^{-1}, is lower than that of the conventional HPDLC due to the low interface energy between liquid crystal molecules and polymer chains.

Figures 5(c) and 5(d) show the response curves of the transmitted light intensity through the cell at room temperature (21 °C). The rise time is 720 μs and the decay time is

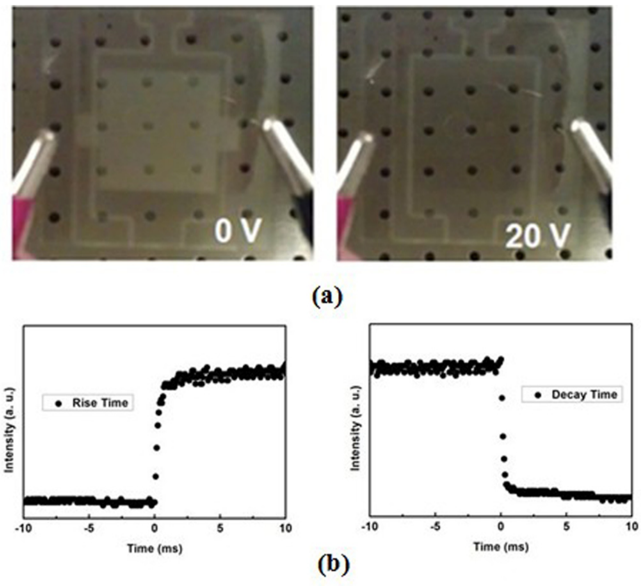

FIG. 5. (a) A light scattering state without electric field, (b) a transparent state with electric field of 4.4 V μm^{-1}. Electro-optical response curves of the switchable film in (c) the rise and (d) decay processes on application of 4.4 V μm^{-1}.

430 μs, which are about one-tenth of the conventional PDLC.[5] The fast response originates from the short pitch length induced by chiral doping.

A liquid crystal phase, sphere phase, is observed in a narrow temperature range between Iso and BP or between Iso and N*. The sphere phase is formed by highly fluid self-organized 3-DTSs and disclination among 3-DTSs based on a balance between the intermolecular interaction and the topological requirement in highly chirality liquid crystal. The temperature range of SP can be broadened to more than 85 °C by stabilizing the disclinations with polymer networks. PS-SPLC is shown sub-millisecond switching time under a low switching electric field of 4.4 V μm^{-1}, promising potential applications in displays, 3D tunable photonic crystals, and phase modulators.

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