SUPPORTING INFORMATION

Fabrication and photonic applications of large-domain blue phase

films

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1. POM images and reflectance spectra of the BP samples (Figure S1-S4).

Herein, a series of comparative experiments were carried out to investigate the effect of each ingredient on BP textures, reflection band gaps and temperature ranges of the samples.



Figure S1. Characterization of BP samples consisting of HTG135200 and R5011. (a) Chemical composition of the samples and chemical structure of R5011. (b) UV-Vis reflection spectra, for samples of S1-1, S1-2 and S1-3, with reflection bandgap at 489, 544 and 609 nm respectively. (c) POM images. Sample S1-1, S1-2 and S1-3 showed blue, green and red color, respectively. The selective reflection of BP samples could be readily predetermined by varying the content of chiral molecule (R5011) in liquid crystal mixtures. Although these BP samples showed vivid structure colors, their temperature ranges were only about 5 °C.



Figure S2. Characterization of BP samples consisting of HTG135200, R5011 and C6M. (a) Chemical composition. (b) UV-Vis Reflection spectrum. (c) POM images. Clearly, all of samples could self-assembly into BPs when varying the content of C6M and HTG135200, it can be observed by reflection spectrum and POM images. As indicated that nematic liquid crystal that the composition of HTG135200 can be replaced by reactive mesogen (C6M) due to its mesogenic property.

(a)	Sample NO.	C6M	R5011
	S3-1	96.5 %	3.5 %



Figure S3. Characterization of BP samples consisting of C6M and R5011. (a) Chemical composition. (b) UV-Vis Reflection spectrum. (c) POM image. Sample S3-1 composed of C6M and R5011 can self-assemble into a BP. C6M could be nematic liquid crystal host in BP structures, revealing that DTCs of BP can be self-assembled by C6M and R5011.

(a)		TITICAL	Dente	aar	TIOTA	(b) 580						
``	Sample	HTG135200	R5011	С6М	TMPIA	(~) 500						
	NO.		100 %	D		560	Ľ					
	S4-1	56.5 %	3.5 %	40.0 %	0 %	Ē				т	I	ł
	S4-2	56.5 %	3.5 %	35.0 %	5.0 %	는 도 ⁵⁴⁰	- 1			I	I	
	S4-3	56.5 %	3.5 %	30.0 %	10.0 %	bue roo	ŀ	I				
		1	.00%			9 520 N	[1				
	S4-4	61.5 %	3.5 %	35.0 %	0 %	Š 500	-		Ŧ			
	S4-5	61.5 %	3.5 %	35.0 %	5.0 %		·					
	S4-6	61.5 %	3.5 %	35.0 %	10.0 %	480	S4-1	S4-2	S4-3	S4-4	S4-5	S4-6

Figure S4. Characterization of BP samples consisting of HTG135200, R5011, C6M and TMPTA. (a) Chemical composition. (b) Reflective wavelengths of different samples.

For samples S4-4, S4-5 and S4-6, only varying the content of TMPTA plays little effect on the change of stopband. All of above results revealing that DTCs of BP were assembled by HTG135200, R5011 and C6M, without TMPTA. TMPTA was speculated to fill in BP disclination cores, rather than DTCs.

For samples of S4-1, S4-2 and S4-3, varying the content of C6M plays an important effect on the change of the stopband of the sample.

			HTG	HTG135200		R5011		N	ТМРТА							
				96.5	96.5-x-y (%) 3.5 (%)		y (%)		x (%)							
Phase Transition (°C)			ТМРТА													
		x = 0		x = 2		x = 4		x = 6		x = 8		x = 10		x = 12		
	y = 0	94.1	89.2	83.4	77.1	76.2	69.0	67.0	58.4							
	y = 10	96.2	91.8	86.9	81.0	79.6	72.8	69.9	61.2	65.9	55.3					
	y = 20	100.4	96.5	90.1	84.8	83.4	76.9	73.7	65.8	67.6	57.4	62.9	47.4			
C6M	y = 30	103.8	100.7	93.3	88.9	86.9	80.9	77.9	69.5	71.1	60.2	64.8	49.7	58.2	35.5	
	y = 40	105.6	103.1	97.3	92.7	89.4	83.3	81.4	73.1	74.4	64.0	67.3	52.0	59.9	37.6	
	y = 50	107.3	105.1	99.0	94.9	91.1	85.3	83.8	75.8	76.9	67.4	69.1	54.3	62.4	39.4	
	y = 60	109.1	107.4	100.4	97.3	93.3	88.0	85.5	77.9	78.8	69.9	71.0	56.4	63.7	42.4	
										Clear HTG1 C6M	ing poi 35200 9 119 °C	nt: 96 °C		Iso.	↔ BP ↔ N*	

2. Temperature range of the BP samples (Figure S5-S10).

Figure S5. Phase transition points (Isotropic phase to blue phase, blue phase to cholesteric phase) of each sample. In this case, BP temperature range of each sample was the difference between the two temperature points.



Figure S6. Phase diagram of the samples according to the data in Figure S5. Clearly, there is little change for the BP temperature ranges of samples when increasing

C6M content (keeping TMPTA content constant), which suggested that C6M could not stabilize the BP structures.



Figure S7. Phase diagram of the samples according to the data in Figure S5. Clearly, there is an obvious increase for the BP temperature ranges of sample when increasing TMPTA content (keeping C6M content constant), suggesting that TMPTA could stabilize the BP structures. TMPTA was speculated to fill in BP disclination cores.

(a)	Sample NO.	HTG135200	R5011	C6M	ТМРТА	
	S8-1	90.5 %	3.5 %	0 %	6.0 %	



Figure S8. (a) Chemical composition of sample S8-1. (b) POM images of samples during the cooling process.

Sample S8-1 showed a phase sequence of Iso-(67.0 °C)-BP-(58.4 °C)-N* on cooling. The temperature range of sample was 8.6 °C. It was found that the suitable amount of

TMPTA broadened BP temperature range even if in the absence of C6M in the mixture. But BP would disappear if the content of TMPTA was more than 6.0 wt% in the system. It may be attributed that too much TMPTA destroyed the BP self-assembly process.



Figure S9. (a) Chemical composition of sample S9-1. (b) POM images of samples during cooling process. Sample S9-1 showed a phase sequence of Iso-(58.2 $^{\circ}$ C)-BP-(35.5 $^{\circ}$ C)-N* on cooling.

Clearly, the BP temperature range was 22.7 °C. there is an enhanced influence for TMPTA on broadening the BP temperature range of sample when C6M content was 30.0 wt% in the mixture. If the content of TMPTA was more than 12.0 wt% in the system, BP would disappear since too much TMPTA destroyed the BP self-assembly process.



Figure S10. The possible illustration of self-organized 3D BP structure. HTG135200, C6M and R5011 assembled into DTCs, TMPTA in the disclination cores could stabilize the BP structures.



3. Photopolymerization of the samples without C6M (Figure S11).

Figure S11. (a) Chemical composition of samples of S11-1, S11-2 and S11-3. (b) POM images of samples before and after UV polymerization. (c) Unit cell of BPI with the independent disclination lines shown in red.

Before polymerization, TMPTA located in the independent disclination lines, keeping the vivid texture of BP. When the photopolymerization happened, there disappeared for BP texture, it may be attributed that TMPTA polymerized with each other into an integral network, leading to DTCs collapsed.

4. The influence of other non-mesogenic monomers (HDDA and EHMA) on the BP samples (Figure S12, S13)

Beside of TMPTA, the phase diagram about 1,6-Hexanediol diacrylate (HDDA) or 2-Ethylhexyl methacrylate (EHMA) was also divided into three regions, but the area of the region II was smaller than that of TMPTA, and the area of EHMA was smallest. In addition, all of these cross-linking agents broadened BP temperature range, and TMPTA showed the optimized broadened effect, which suggested that the stabilization effect of crosslinking agent in BP might be associated with a branched structure of the side alkyl group in the polymer.



Figure S12. (a) Chemical structure of HDDA. (b) Phase diagram of the samples with chemical composition of HTG135200 / R5011 / C6M / HDDA / I-651 = 96.0-x-y / 3.5 / x / y / 0.5 (wt%).

The phase diagram was divided into three regions (I, II, III), which was similar to that of Figure 2a. (c) BP temperature range of the samples before photopolymerization with chemical composition of HTG135200 / R5011 / C6M / HDDA / I-651 = 66.0-x-y / 3.5 / 30 / x / 0.5 (wt%).



Figure S13. (a) Chemical structure of EHMA. (b) Phase diagram of the samples with chemical composition of HTG135200 / R5011 / C6M / EHMA / I-651 = 96.0-x-y / 3.5 / x / y / 0.5 (wt%). The phase diagram was divided into three regions (I, II, III), which was similar to that of Figure 2a. (c) BP temperature range of the samples before photopolymerization with chemical composition of HTG135200 / R5011 / C6M / EHMA / I-651 = 66.0-x-y / 3.5 / 30 / x / 0.5 (wt%).

5. Domain size and the corresponding reflectance intensity of the samples as a function of TMPTA content (Figure S14, S15).



Figure S14. (a) Chemical composition of samples (20 wt% C6M in the mixture). (b) POM images of samples before and after UV polymerization with TMPTA content varying from 0 to 10 wt%. (c) Domain sizes of BPI platelets when varying the content of TMPTA in mixtures. (d) Reflection intensity of the samples before and after UV polymerization. The domain size and the reflection intensity reached the maximum value for the sample with 3 wt% TMPTA, 20 wt% C6M.



Figure S15. (a) Chemical composition of samples (40 wt% C6M in the mixture). (b) POM images of samples before and after UV polymerization with varying the content of TMPTA from 0 to 12 wt%. (c) Domain sizes of BPI platelets when varying TMPTA content in mixtures. (d) Reflection intensity of the samples before and after UV polymerization. The domain size and the reflection intensity reached the maximum value for the sample with 6 wt% TMPTA.40 wt% C6M in the system.



6. Schematics of self-assembly process (Figure S16-S18).

Figure S16. (a) Chemical composition of the sample in Figure 3. (b) POM images in Figure 3. (c) Scheme of the BP self-assembly processes based on the experimental observation. Where, the blue and green blocks stand for BPII and BPI assembled by mesogens (HTG135200, C6M, R5011) and the red dots stand for TMPTA. The blocks

that self-assembled into uniform orientation stand for a BP domain. TMPTA was beneficial to the elimination of grain boundaries of BPII domains during self-assembly process, resulting in large-domain BPs.



Figure S17. (a) Chemical composition of sample S17-1. (b) POM images of the sample when cooling from 82.0 °C to 78.0 °C at 0.1 °C/min, some important features of the growth process of BP are captured at 81.7 °C, 81.6 °C, 81.5 °C, 81.0 °C and 80.5 °C, respectively. (c) Scheme of the BP self-assembly processes based on the experimental observation. TMPTA was too low to fill the disclination cores. It is difficult to eliminate the grain boundaries of BPII domains during self-assembly process, leading to smalldomain BPs.



Figure S18. (a) Chemical composition of sample S18-1. (b) POM images of the sample when cooling from 68.0 °C to 58.0 °C at 0.1 °C/min, some important features of the growth process of BP are captured at 66.8 °C, 66.0 °C, 65.0 °C, 64.0 °C and 63.5 °C respectively. (c) Scheme of the BP self-assembly processes based on the experimental observation. It was affected for the elimination of grain boundaries of BPII domains by too much TMPTA during self-assembly process, resulting in small-domain BPs.

7. Temperature range of the BP film (Figure S19, S20).

The texture of the BP film kept from -40 °C to 180 °C. Differential scanning calorimetry (DSC) curve of the sample showed that no phase transition occurred during the temperature window.



Figure S19. (a) Chemical composition of sample S19-1. (b) POM images of sample when cooling from -40 °C to 180 °C, it is clarified that the structure persists over a range of at least 220 °C.



Figure S20. (a) Reflection spectra of the film at different temperature. The reflection intensity firstly increased and then decreased when varying the temperature from -40 $^{\circ}$ C to 180 $^{\circ}$ C, suggesting a possible glass transition at lower temperatures and a gradual transition to the isotropic phase at higher temperatures. (b) DSC curve of the BP film, it is determined at the cooling/heating rate of 20 $^{\circ}$ C/min.

8. TEM characterization (Figure S21)



Figure S21. TEM images of samples in different magnifications. (a) 2.0 k. (b) 5.0 k.