Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Towards complete photonic band gap in a high refractive index nanoparticle-doped blue phase liquid crystal

Nurjahan Khatun[a, b], Vimala Sridurai[a, c] and Geetha G. Nair[a*]

[a] Centre for Nano and Soft Matter Sciences, Bangalore 562162, India

[b] Manipal Academy of Higher Education, Manipal 576104, India

[c] Present address: Laboratoire Charles Coulomb, UMR 5221, CNRS-Université de Montpellier, F-34095 Montpellier, France.

* E-mail: geeraj88@gmail.com and ggnair@cens.res.in

S1. FEM simulation:

Models used

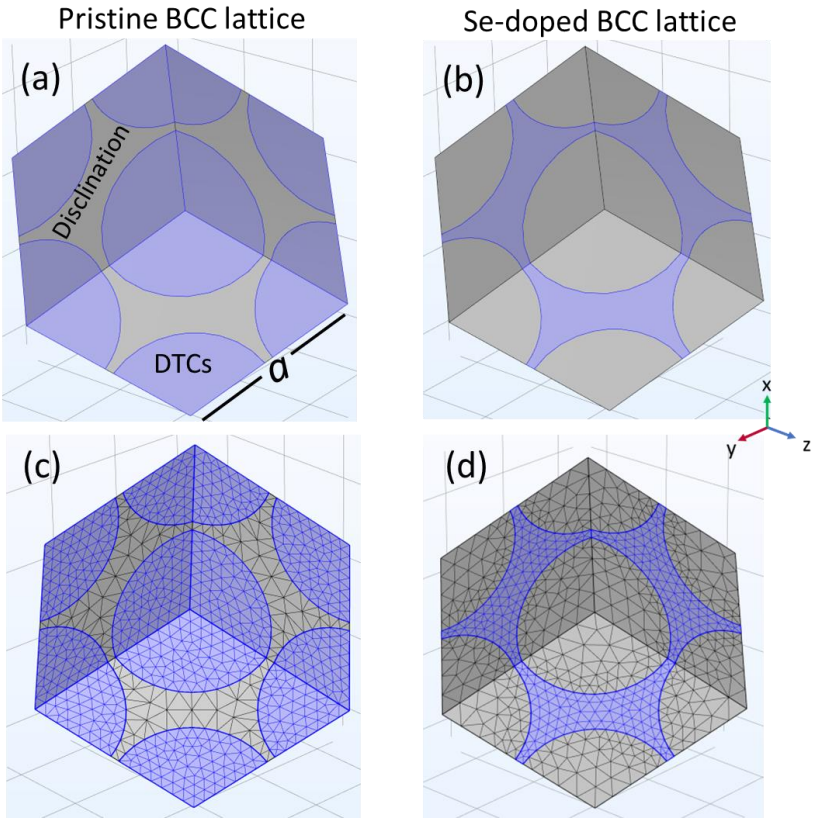


Figure S1. *Primitive unit cell used for photonic band diagram simulation corresponding to the BCC lattice of (a) Pristine BP and (b) Se-BP systems. The spheres and surrounding regions in the lattice represent the DTCs and disclinations, respectively. The mesh pattern used in the model for Pristine BP and Se-BP are shown in (c) and (d).*

Reflection studies: Electric field distribution

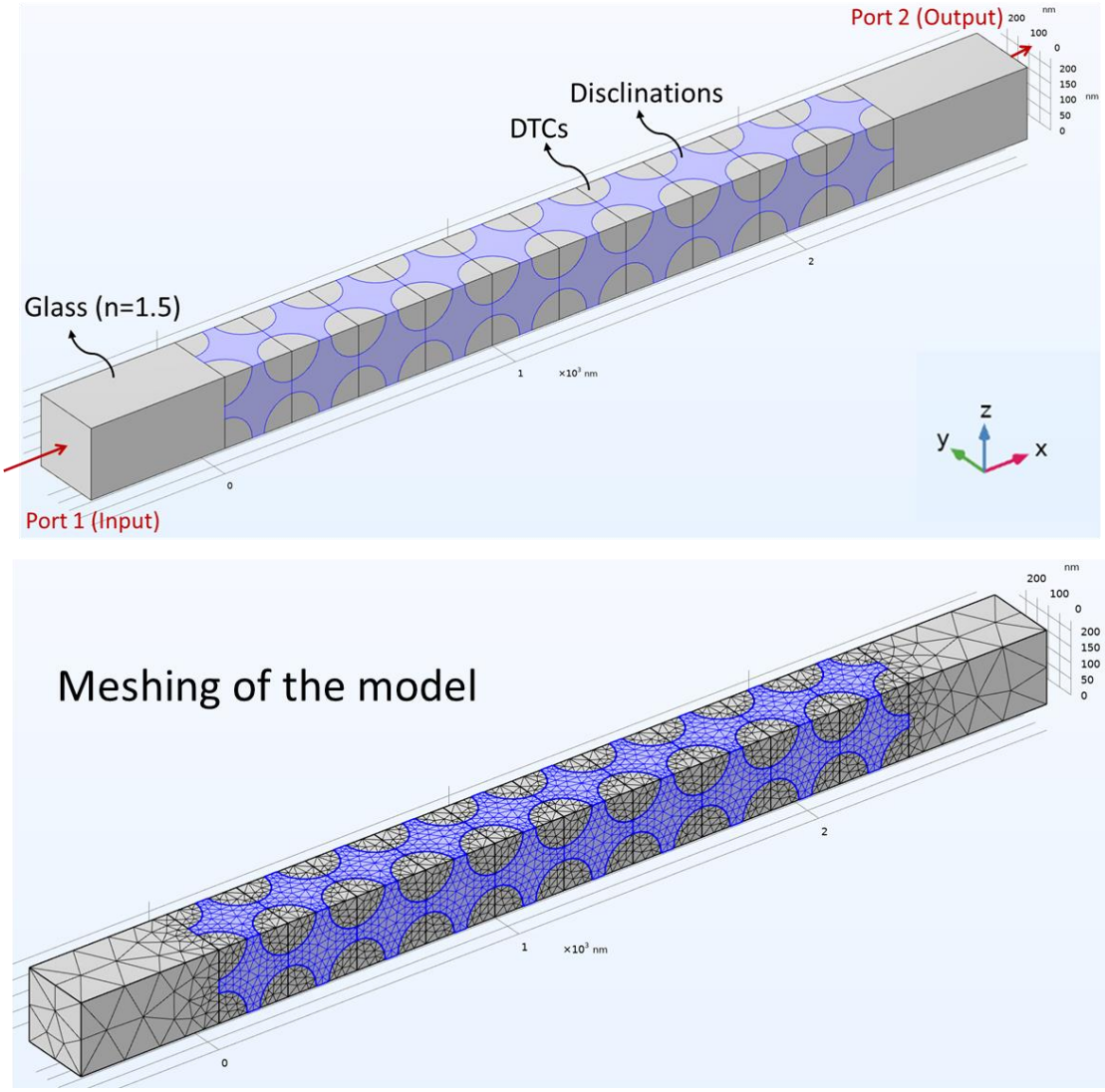


Figure S2. *10 unit cells of the conventional BCC lattice used for simulating reflection spectra (top). The light propagates along x direction and polarized along y-z direction. Bottom image depicts the meshing of the model.*

For both the Pristine BP and Se-BP systems, the electric field propagation is more at the edges of the photonic band gap due to the presence of high density of states (DOS) [S1] as shown in **Figure**

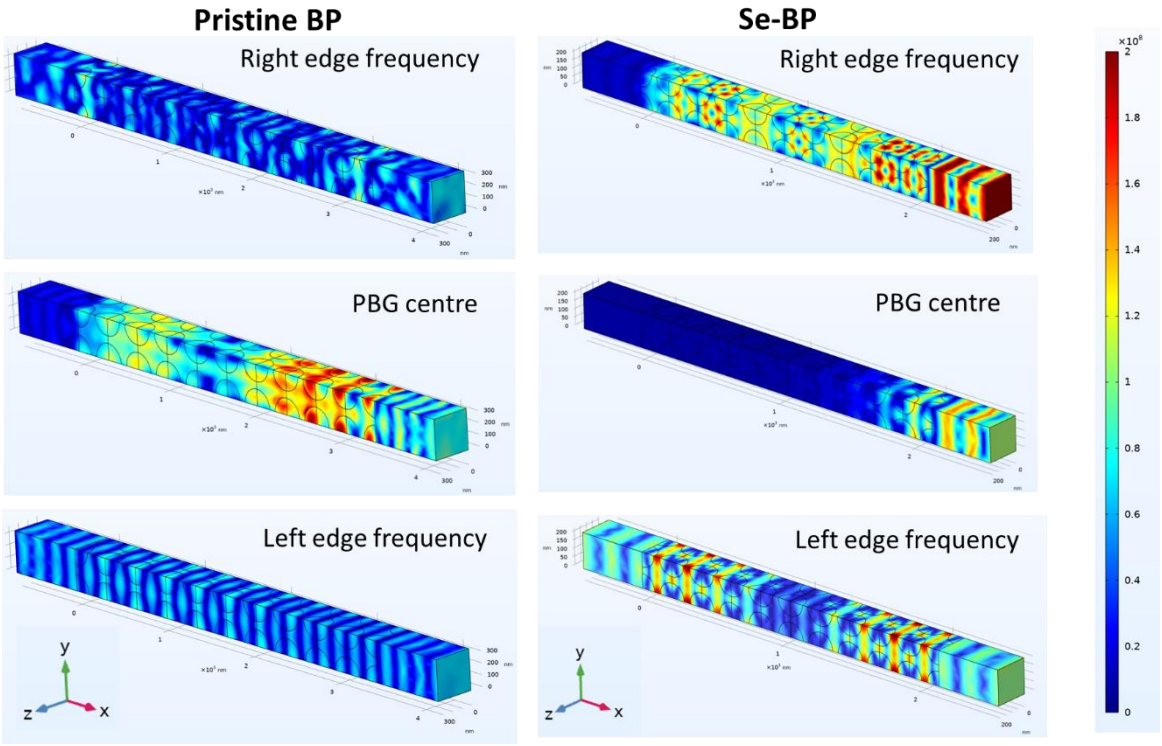


Figure S3. *Simulated eigen mode electric field distribution at the centre of PBG and the band edges for the Pristine BP and Se-BP systems.*

S3. Additionally, the electric field confinement is more at the higher frequency band edge, confirming the non-linear dispersion of the DOS in the photonic crystal.[S2, S3]

The attenuation of EM wave (**Figure S3**) and the electric field enhancement in the high dielectric medium of Se-BP (see **Figure 1**) can be explained as follows: In the Pristine BP, the refractive index contrast or difference (Δn) between the DTCs and disclination lines is only 0.04 (i.e., $n_{DTC} - n_{Disclination}$= 1.6-1.56).[S4, S5] In the Se-BP, the Se particles are trapped in the core of disclination lines, and therefore the Δn is 1.47 (i.e., $n_{Disclination} - n_{DTC}$ = 3.07 - 1.6). Due to the enhancement in Δn, the electric field confinement is higher, resulting in attenuation of EM wave propagation which in turn leads to widening of band gap in the Se-BP.

S2. Synthesis of Se nanoparticles (Se NPs)

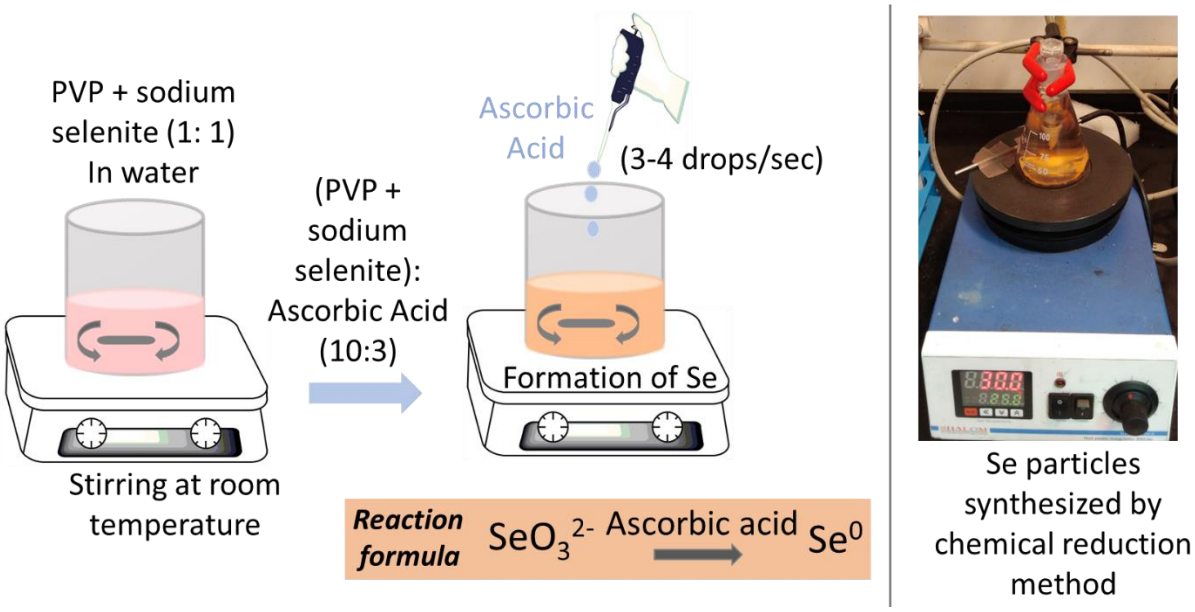


Figure S4*. Schematic representation of the synthesis route used for preparation of Se NPs. The synthesis is done at ambient conditions.*

S3. Characterization of Se NPs

Particle size distribution and EDAX :

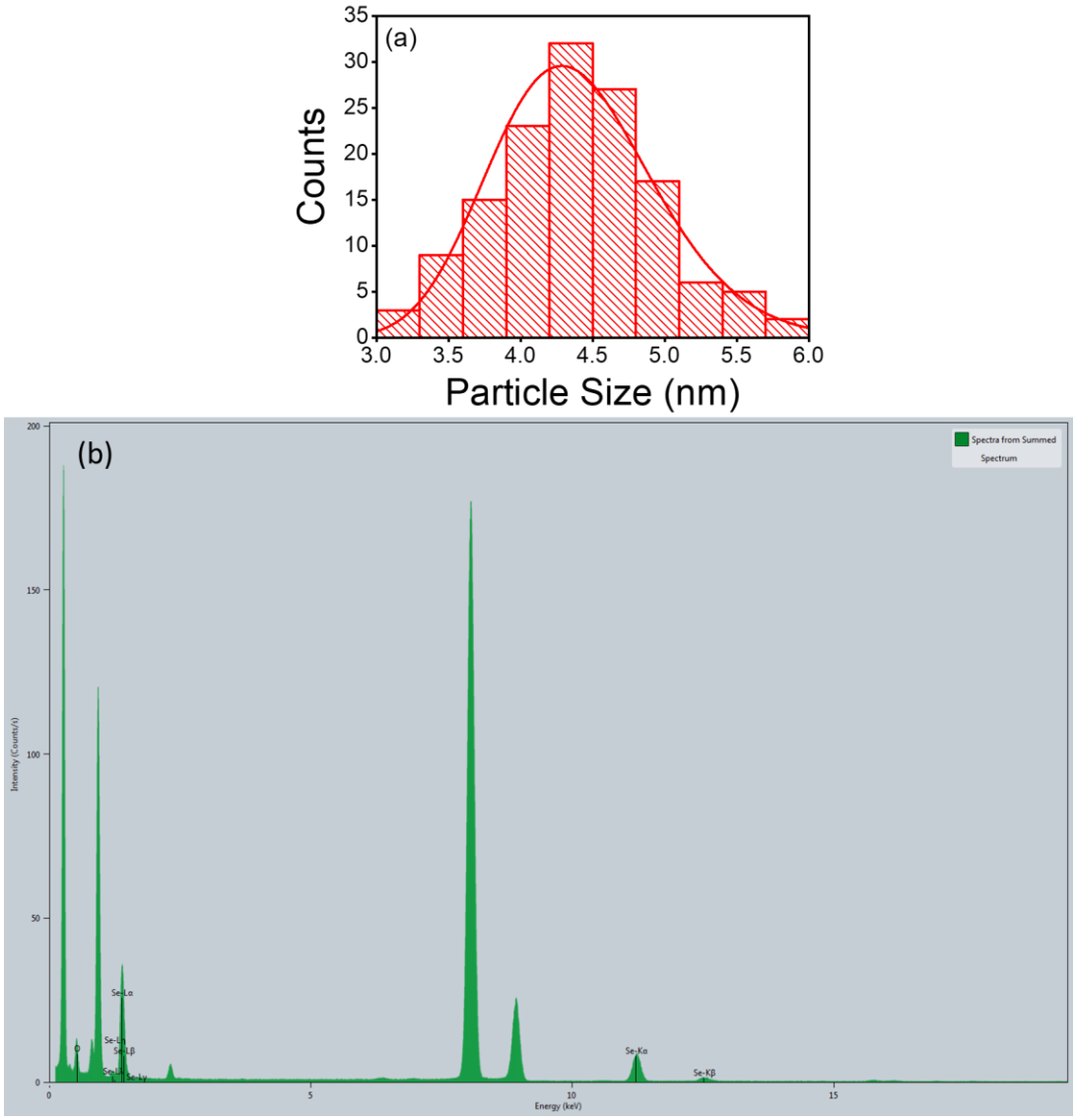


Figure S5. *(a) Particle size distribution and (b) Energy dispersive X-ray analysis (EDAX) of the Se NPs obtained from HRTEM. The average size of the particles is 4.3 ± 0.5 nm (calculated using Image J software).*

X-ray diffraction (*XRD) of Pristine BP and 5%Se-BP:*

XRD experiments carried out in the BPI for Pristine BP and 5%Se-BP at a fixed temperature of 30 ^{o}C are shown in Figure S7. The data for Pristine BP shows a single broad peak at wide angles (2θ=20.396), characteristic of fluid-like ordering. No peak is seen at low angles as BP does not possess any positional order. The XRD profile obtained at wide angles for Se-BP consists of crystalline peaks corresponding to Se NPs (See **Figure 3d**, main manuscript) in addition to the broad peak (2θ=20.126) corresponding to the fluid-like ordering of BPI (see **Figure S6**).

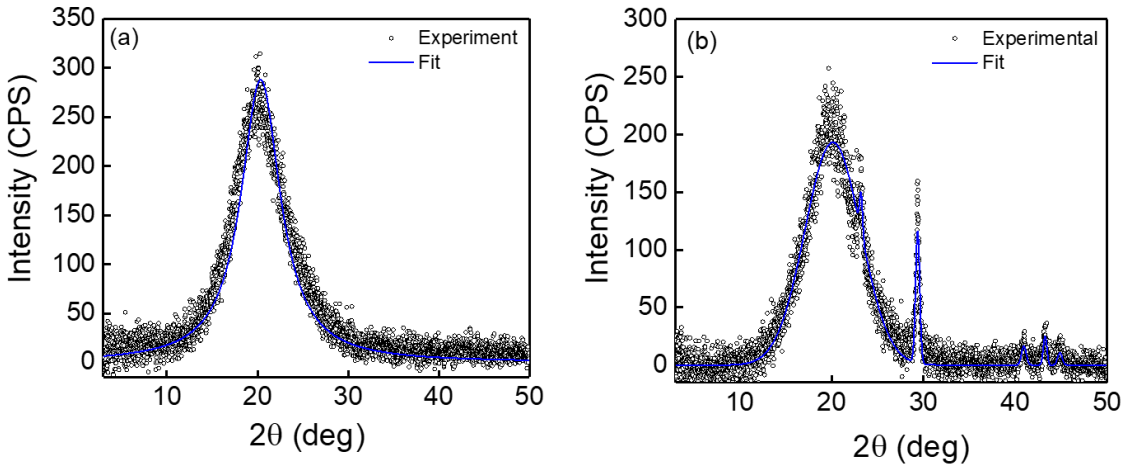
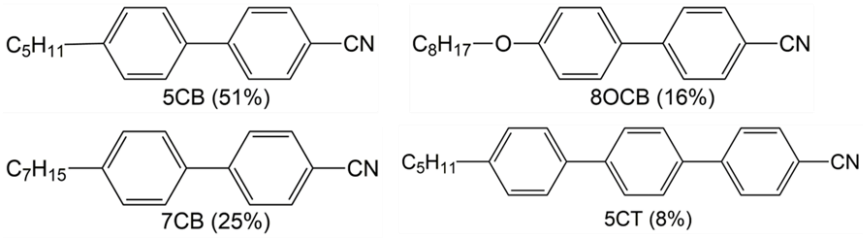


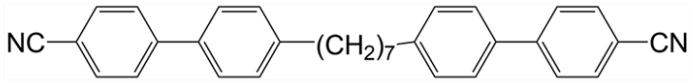
***Figure S6**. The XRD profiles obtained for (a) Pristine BP and (b) 5%Se-BP at 30 °C in BPI.*

S4. Chemical structure, phase sequence and phase transition temperatures of the constituent compounds used for the preparation of BP composites

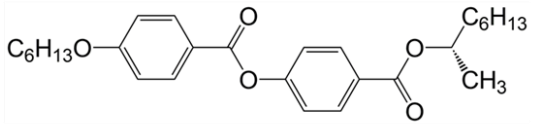
E7 *(Iso 59 °C N -51 °C Cr)*



CB7CB *(Iso 115.3 °C N 103 °C N_{TB})*



S811 *(Iso 51 °C Cryst)*



Composites:

1. 52 wt% NLC + 28 wt% S811 + 20 wt% NTB (Pristine BP)
2. 0.2 to 5 wt% of Se NPs in Pristine BP : X% Se-BP, where X = 0.2, 0.5, 1, 2 and 5

Phase sequence:

1. Pristine BP: Iso 38.6 °C BPIII 38.2 °C BPI 25 °C Ch
2. X% Se-BP: Iso 39 °C BPIII 38.6 °C BPI 25 °C Ch

Figure S7*. Chemical structure and phase transition temperatures of the individual compounds that constitute the BP composites. The compositions and phase sequence of the composites are also shown.*

S5. Platelet textures and time-dependence growth of BPI

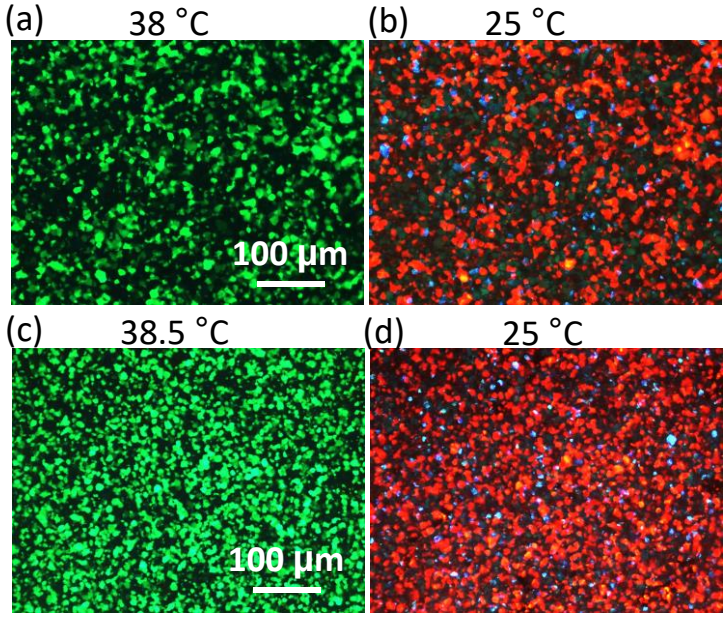


Figure S8. *The characteristic platelet textures of BPI obtained at 38 °C and 25 °C for Pristine BP (a, b) and at 38.5 °C and 25 °C for 5%Se-BP (c, d). The samples are cooled to the BPI at the rate of 0.2 °C/min from the isotropic phase through BPIII.*

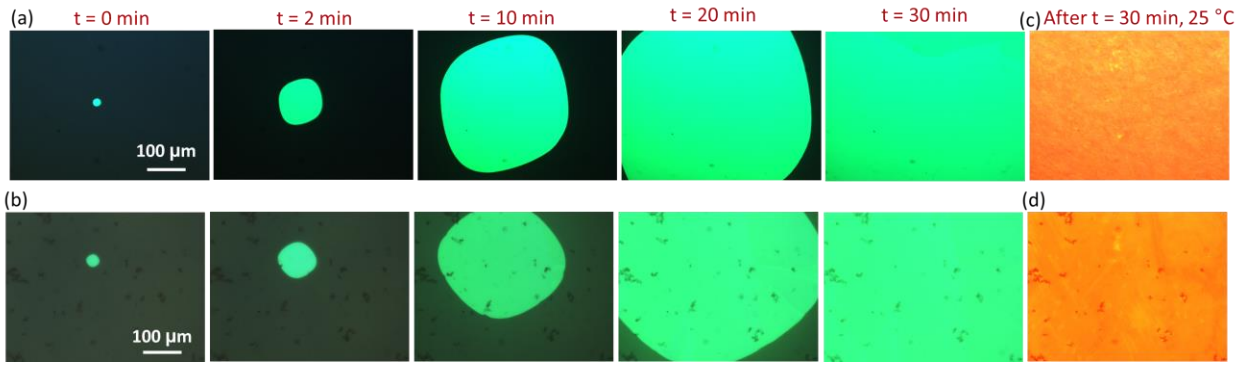


Figure S9*. Time-dependence growth of BP platelets when the sample is held at a constant temperature of 38.2 °C (Pristine BP) and 38.6 °C (Se-BP), just when a tiny crystallite of BPI appears in the field of view at the onset of BPIII to BPI transition for (a) Pristine BP and (b) 5%Se-BP. At the end of ~ 30 mins large monodomains form in both cases. (c) and (d) shows the monodomains reflecting red colours (red-shift) as the samples are cooled further in the BPI.*

S6. Kossel diagrams

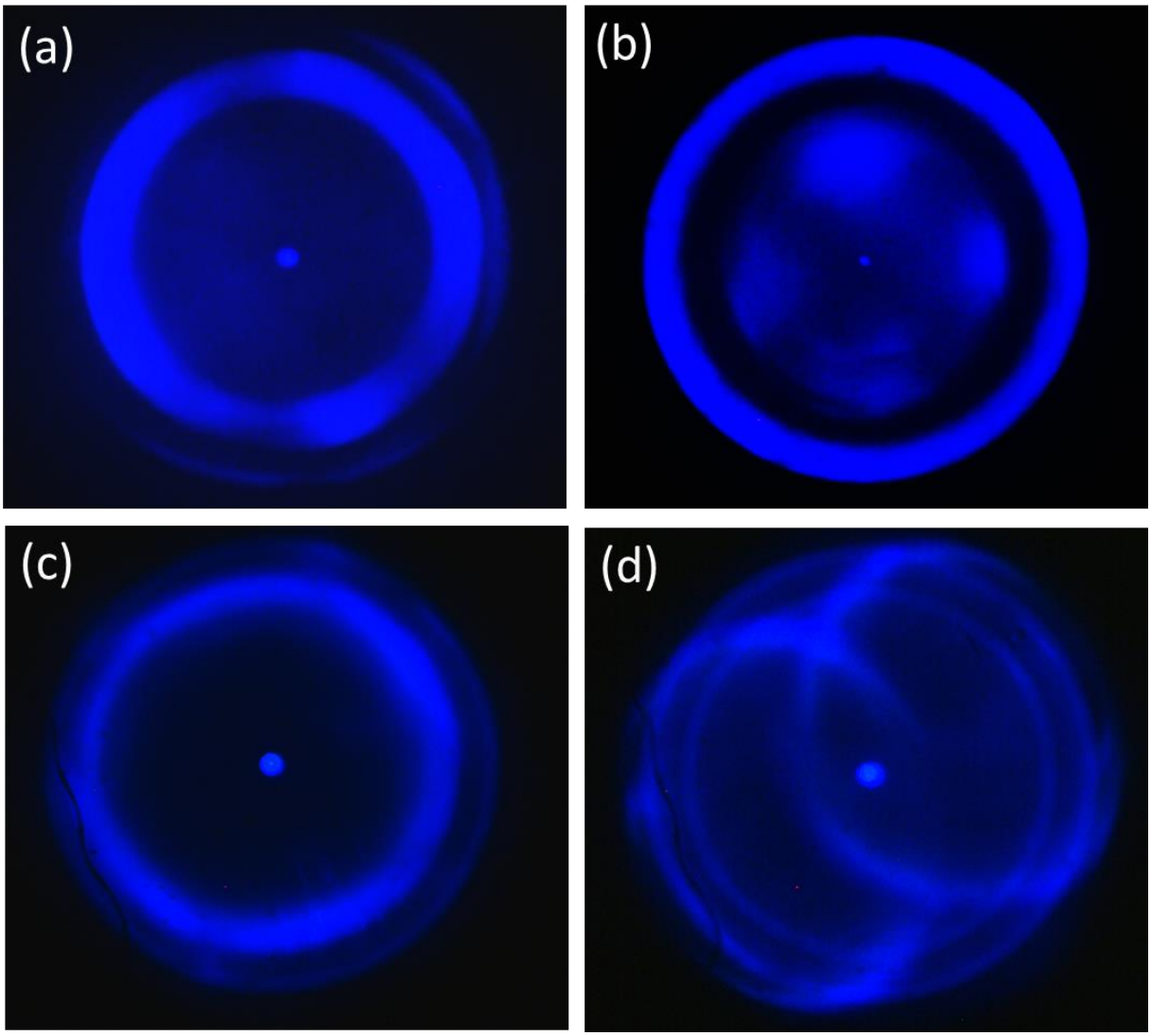


Figure S10*. Kossel diagrams for Pristine BP (a & b) and Se-BP (c & d) confirm the presence of (110) plane of BPI.*

S7. Band diagram and reflection spectra of Se-BP with n_{DTC} =1.6 and $n_{Disclination}$ = 2.3

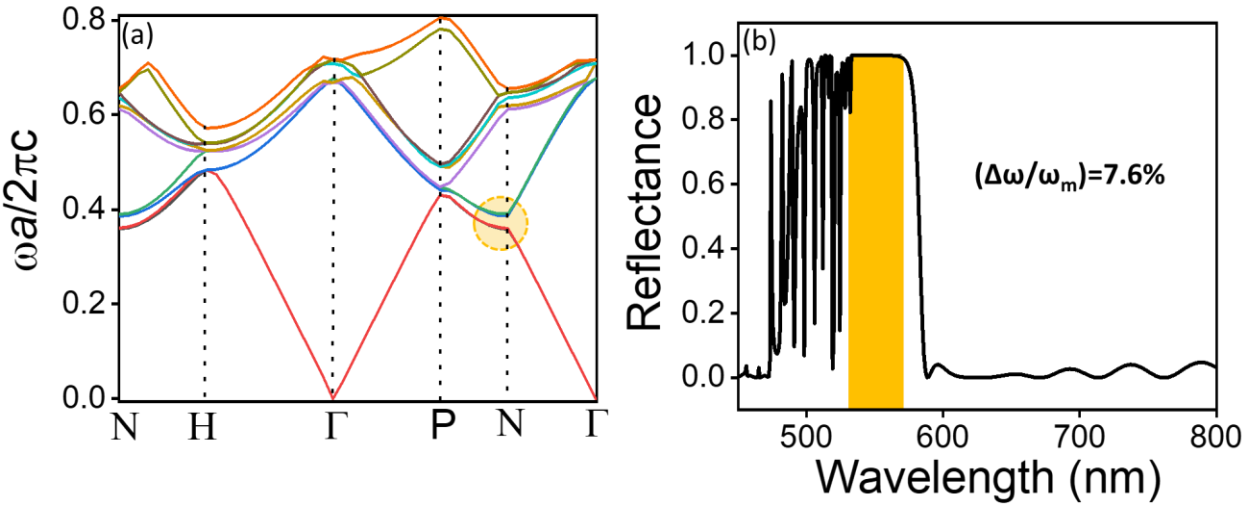


Figure S11. *The simulated (a) band diagram and (b) reflection spectra of Se-BP when the refractive index of the medium is chosen as 1.6 (n_{DTC}) and 2.3 ($n_{Disclination}$). The calculated PBG width of 7.6% is in close agreement with experimentally determined value of 5.6%.*

S8. Selective reflection studies of the BP composites, X%Se-BP

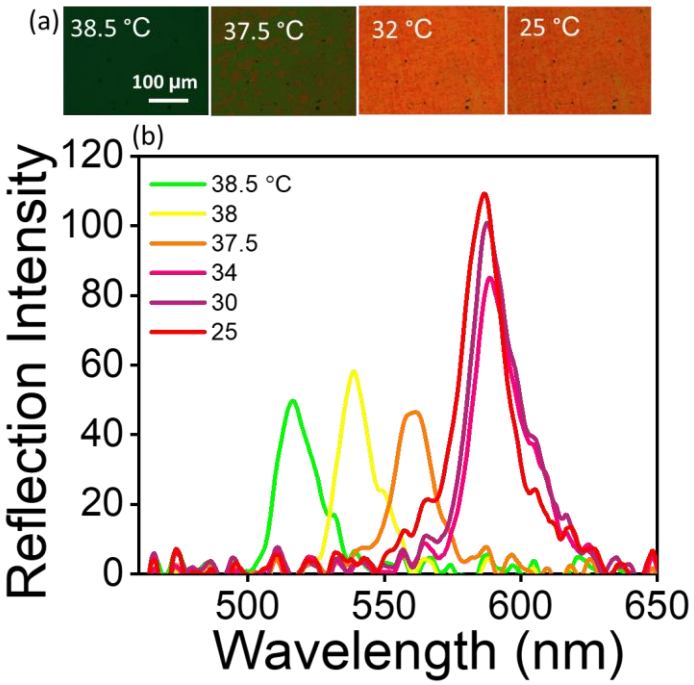


Figure S12. *(a) POM textures and (b) reflection spectra of 0.2%Se-BP composite at different temperatures in BPI.*

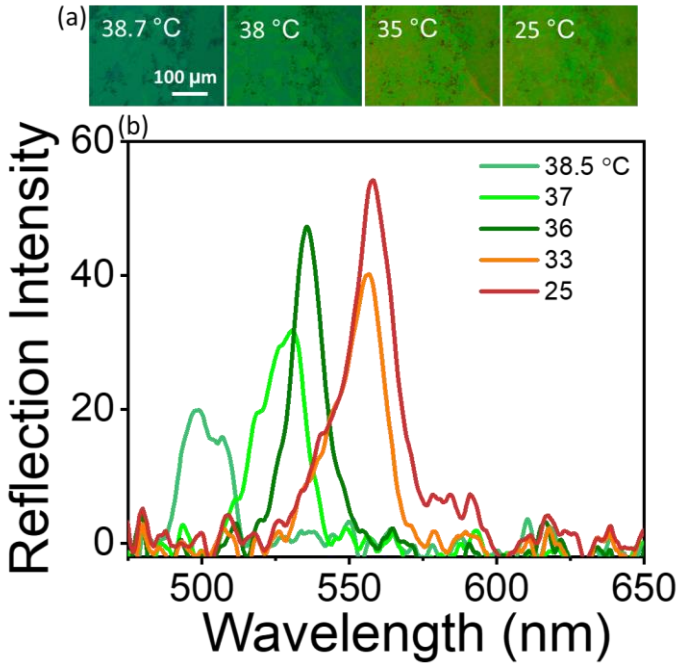


Figure S13. *(a) POM textures and (b) reflection spectra of 0.5%Se-BP composite at different temperatures in BPI.*

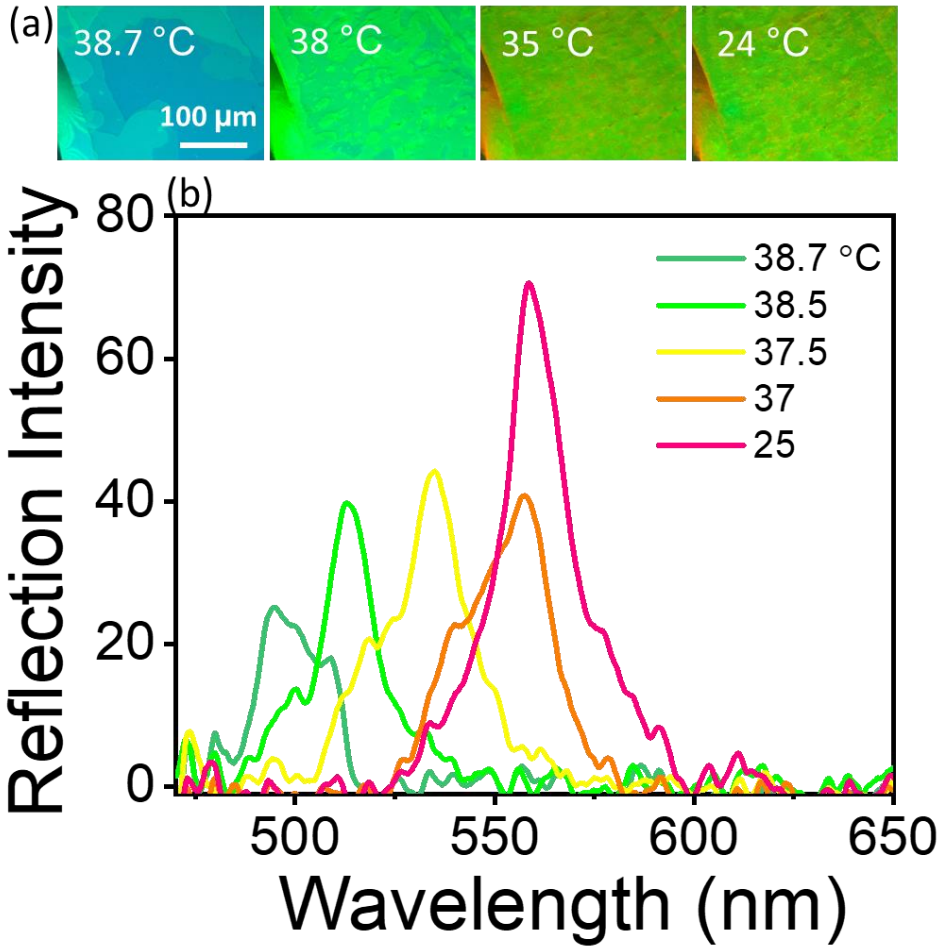


Figure S14. *(a) POM textures and (b) reflection spectra of 1%Se-BP composite at different temperatures in BPI.*

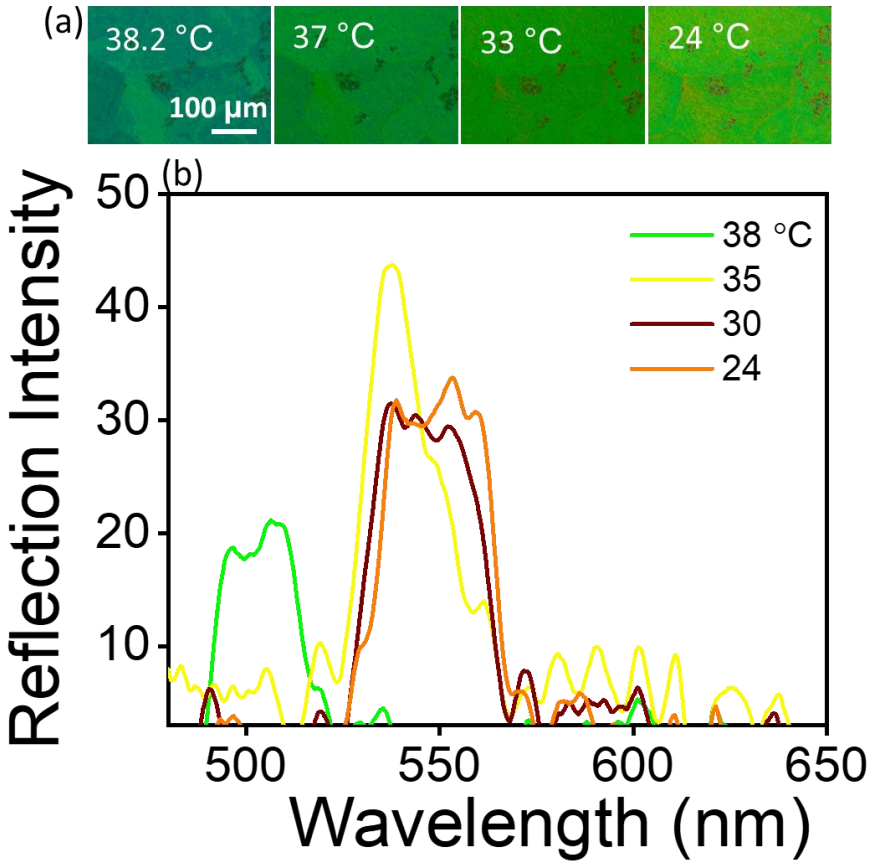


Figure S15. *(a) POM textures and (b) reflection spectra of 2%Se-BP composite at different temperatures in BPI.*

The textural images along with selective reflection spectra obtained for X% Se-BP where X=0.2, 0.5, 1 and 2 are shown in **Figures S12-S15**. All the composites exhibit similar phase sequence as that of Pristine BP, i.e., Iso-BPIII-BPI upon cooling from Iso. It may be noted here that Se NPs doping in BP hardly affects the transition temperatures. The spectra show that the PBG width starts to increase beyond a threshold particle concentration of 0.5%. It is observed that the PBG width hardly varies beyond 1%, and for X% >5, the scattering from the nanoparticles affects the vividness of the reflected colours.

Table S1: Central wavelength (λ_m), and FWHM ($\Delta\lambda$) of selective reflection peaks along with the measured PBG width ($\Delta\lambda$ / λ_m) in BPI for the Pristine BP and X%Se-BP composites.

BP composites	Central Wavelength (λ_m) (nm)	FWHM ($\Delta\lambda$) (nm)	($\Delta\lambda/\lambda_m$) (%)
Pristine BP	557	14.1	2.5
0.2% Se- BP	560	18.3	3.3
0.5% Se- BP	557	21.0	3.8
1% Se- BP	553	30.1	5.4
2% Se-BP	549	30.1	5.5
5% Se-BP	570	31.9	5.6

References:

[S1] P. Lodahl, A. Floris van Driel, I. S. Nikolaev, A. Irman, K. Overgaag, D. Vanmaekelbergh, W. L. Vos, *Nature,* 2004, **430**, 654.

[S2] E. Yablonovitch, *Phys. Rev. Lett.,* 1987, **58**, 2059.

[S3] J. Joannopoulos, S. Johnson, J. Winn, R. Meade, Press, 2008.

[S4] M. Ojima, Y. Ogawa, R. Ozaki, H. Moritake, H. Yoshida, A. Fujii, M. Ozaki, *Appl. Phys. Express,* 2010, **3**, 032001.

[S5] H. Yoshida, K. Anucha, Y. Ogawa, Y. Kawata, M. Ozaki, J.-i. Fukuda, H. Kikuchi, *Phys. Rev. E,* 2016, **94**, 042703.