Supplementary Information

Strain-induced alignment and phase behavior of blue phase liquid crystals confined to thin films

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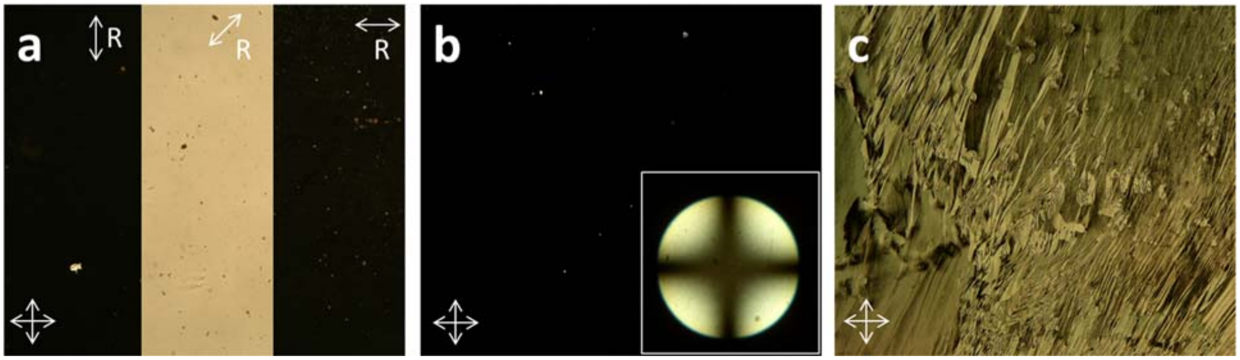

Figure S1 Optical micrographs of ~20 μm-thick films of MLC 2142 confined between surfaces of (a) PVA (rubbed in direction R) (b) DMOAP, and (c) bare glass.

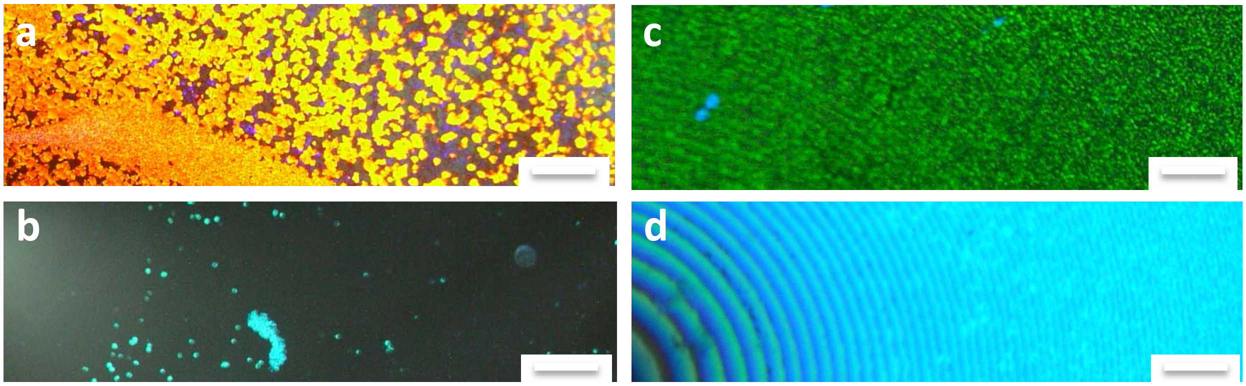

Figure S2. Reflection-mode micrographs (crossed polars) of 35% wt/wt S-811/MLC 2142 in (a, c) BPI or (b,d) BPII, when confined between surfaces of (a,b) bare glass (rubbed) or (c,d) PVA (not rubbed). Scale bar: 200 μm.

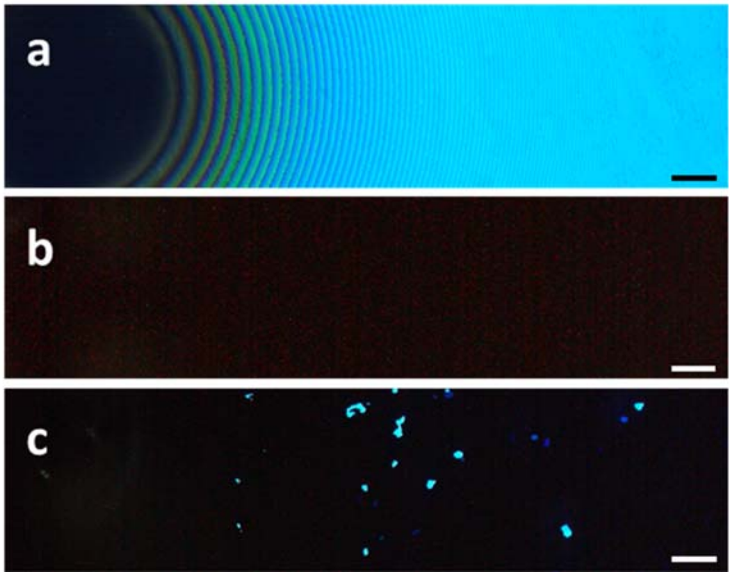

Figure S3 Reflection-mode micrographs (crossed polars) of 35% wt/wt S-811/MLC 2142 in BPII confined between surfaces of **(a)** rubbed PVA, **(b)** DMOAP, **(c)** bare glass. Scale bars: 200 μm.

Calculation of the BP lattice sizes

We calculated the BP lattice sizes and Chol pitch sizes using the UV-vis spectra of the flat films of the LC confined between surfaces of PVA, bare glass, DMOAP (**Figure S3**). The wavelength of light reflected from the specific planes of the BP is determined from minima in %T vs. wavelength spectra and Eqn. (S1),

$$\lambda_{hkl} = \frac{2na}{\sqrt{h^2+k^2+l^2}} \qquad \text{(S1)}$$

The calculated lattice sizes of the BPs are shown in Table S1. The BPI lattice size was estimated as ~253 nm, whereas for BPII it was estimated as ~157 nm. Along with these estimates, the cholesteric pitch was determined as ~300 nm.

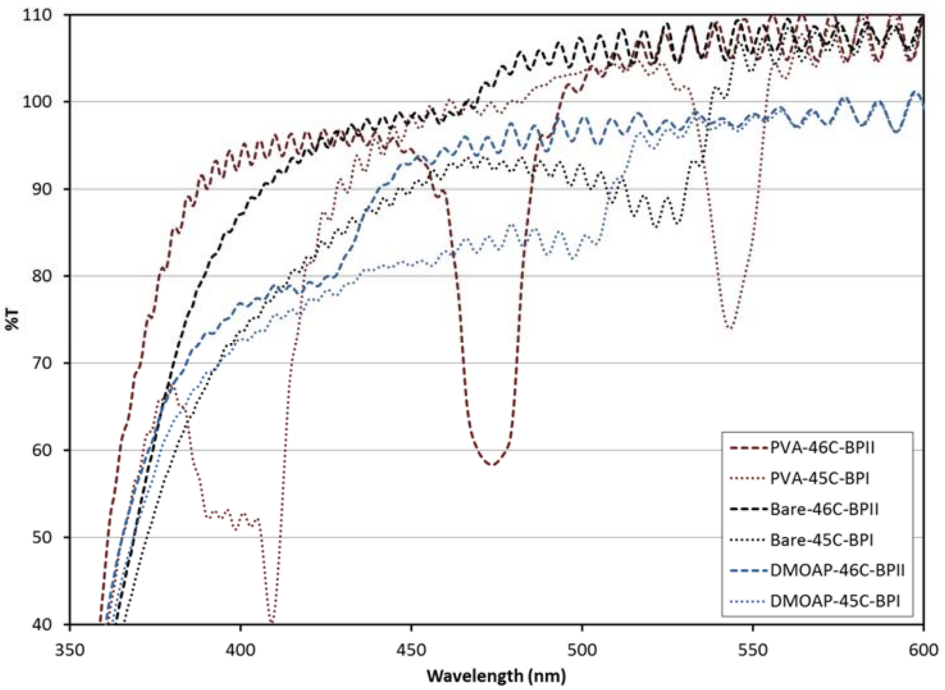

Figure S4 UV-vis transmission spectra using a ~20 µm-thick film of 35 wt% S-811/MLC 2142 sandwiched between rubbed-PVA, bare glass, or DMOAP surfaces, at the temperatures indicated (measurements relative to the isotropic phase).

Table S1. Summary of the Chol pitch, and BP lattice size measurements

Technique	Surface	System	P_{chol}	a_{BPI}	a_{BPII}	Reference
Microscopy	PVA (Rubbed)	PCX	328	283	175	This study
	Bare Glass	PCX	-	290	-	This study
	DMOAP	PCX	-	280	-	This study
UV-VIS	PVA (Rubbed)	Flat	300	270	160	This study
	Bare Glass	Flat	-	250	160	This study
	DMOAP	Flat	-	240	150	This study
Color	Bare Glass (Rubbed)	PCX	300	290	179	Blumel and Stegemeyer[1]
Microscopy	Bare Glass (Rubbed)	PCX	330*	260*	-	Feldman et al.[2]

*calculated from data

Using the unit cell orientations (Figure 4), the optical micrographs and the models sketched in Figure 5, we calculated the unit cell sizes using a model based on the elastic energy, as first proposed by Feldman et al.[2] In this model, only the twist part of the elastic energy expression was used and the locations of the step boundaries, r_d, were estimated as;

$$r_d^2 = \left(m + \frac{1}{2}\right) r_1^2 \qquad \text{(S2)}$$

where m is the integer number of half-pitches, and r_1 is the distance from the center of the PCX optical cell and the location where m = 1. Here we note that although the model Eqn. (S2) was first derived by Feldman et al., they did not use it to estimate the lattice size of the BPs as they did not know the orientation of the BP unit cells. However, from our analysis of the alignment of BPI and BPII and the sketch shown in Figure 5g-h, we used Eqn. (S2) to calculate the lattice parameter of BPI to be 283 nm for PVA, 290 nm for bare glass and 280 nm for DMOAP surfaces, and BPII to be 175 nm (Table 1, Figure S4). The agreements between the measured lattice sizes and literature values, and the estimates from UV-vis spectra clearly indicate the same orientation and organization of BPI at the thin edge of the wedge cells, independent of the chemistry of the contacting surfaces.

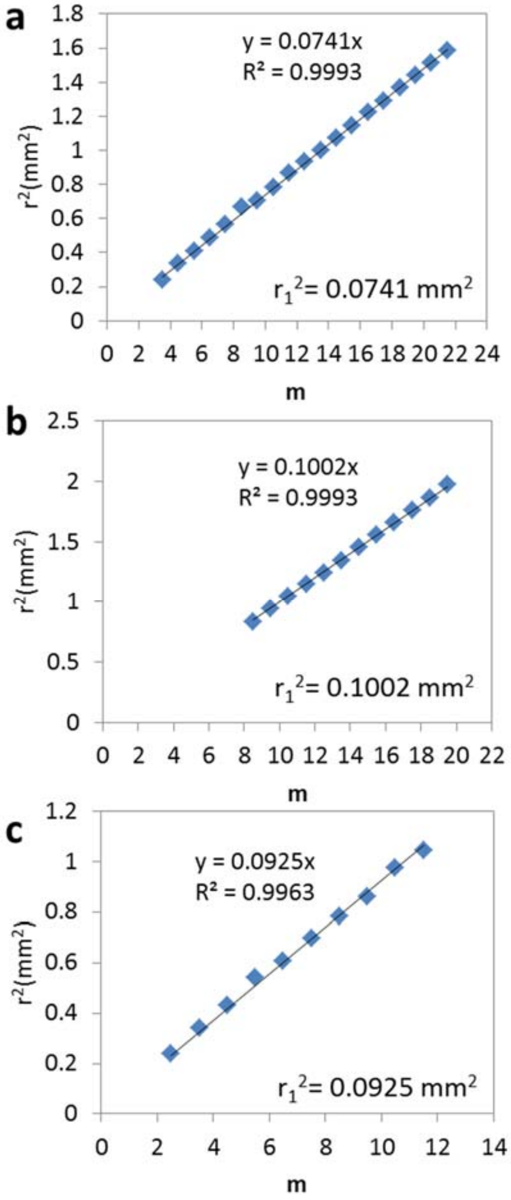

Figure S5 r^2 vs m plots for 35% wt/wt S-811/MLC2142 confined between PVA surfaces (a) Chol, (b) BPI, (c) BPII.

Details of computer simulations

We described the chiral liquid crystal using a continuum mean field Landau-de Gennes approach, where the free energy is given by

$F(Q) = \int_V (f_{LdF}(Q) + f_E(Q))dV + \int_S (f_s(Q))ds,$ (S3)

where the tensorial order parameter, Q, is defined as, $Q = < nn - \frac{1}{3}\delta >$, n is a vector aligned with the long axis of each molecule, and δ is the Kronecker delta.

In Eq. S3, f_{LdF} accounts for the short-range free energy of the form,

$f_{LdF}(Q) = \frac{A}{2}\left(1 - \frac{U}{3}\right) Q_{ij}Q_{ji} - \frac{AU}{3} Q_{ij}Q_{jk}Q_{ki} + \frac{AU}{4}\left(Q_{ij}Q_{ji}\right)^2,$

where A and U are material parameters that capture the thermodynamics of the LC. For a uniaxial system the elastic contribution to the free energy, f_E, is written as follows $f_E = \frac{L}{2}\frac{\partial Q_{ij}}{\partial x_k}\frac{\partial Q_{ij}}{\partial x_k} + 2\,L\,q_0 \epsilon_{ikl} Q_{ij} \frac{\partial Q_{lj}}{\partial x_k}$, where L is the elastic constant, $q_0 = 2\pi/p$ being p the cholesteric pitch. The final term in Eq. S3 describes the interaction of the liquid crystals with the surfaces, for planar degenerate anchoring, it is described by the Fournier and Galatola expression of the form $f_s = w(\widetilde{Q} - \widetilde{Q}^{\perp})^2$, where $\widetilde{Q} = Q + \frac{S}{3}\delta, \widetilde{Q}^{\perp} = P.\widetilde{Q}.P, P = \delta - \nu\nu$. The projection of the tensor on the surface is defined by $\widetilde{Q}^{\perp}$, ν is the normal vector at the surface, and w denotes the strength of the surface anchoring. For planar aligned and for homeotropic anchoring $fs = w(Q-Q_0)^2$, where Q_0 is the tensorial order parameter associated to the preferred director alignment at the surface.

The total free energy is minimized by using the Euler-Lagrange formalism in a lattice array with mesh resolution of 10 nm. Equilibrium conditions for bulk and surface are given as follows:

$$\frac{\partial f}{\partial Q} - \nabla \frac{\partial f}{\partial \nabla Q} = 0 \ \text{(bulk)}, \quad \frac{\partial f}{\partial \nabla Q}.\nu = 0 \ \text{(surface)}.$$

LC parameters were taken to be $L = 2.5\times10^{-11}$ N, $A = 1.02\times10^{5}$ J/m^3. For BPI, U=3.0 and $p = 0.5\ \mu m$ while for BPII, U=2.755 and $p = 0.344\ \mu m$, which give unit cell sizes $a_{BPI} =$

$0.52\ \mu\mathrm{m}$ and $\mathrm{a}_{\mathrm{BPII}} = 0.20\ \mu\mathrm{m}$. Initial conditions where taken from the blue phases ansätze for unit cells oriented with either (200) or (110) planes parallel to the channel surface in the case of BPI; and for BPII with the unit cell oriented with either (100), (110) and (111) parallel to the channel surface. Because of the different simulation box sizes between blue phases with different lattice orientations, the free energy density differences, as compared to the unconfined bulk phase, were compared to determine the stable structure.

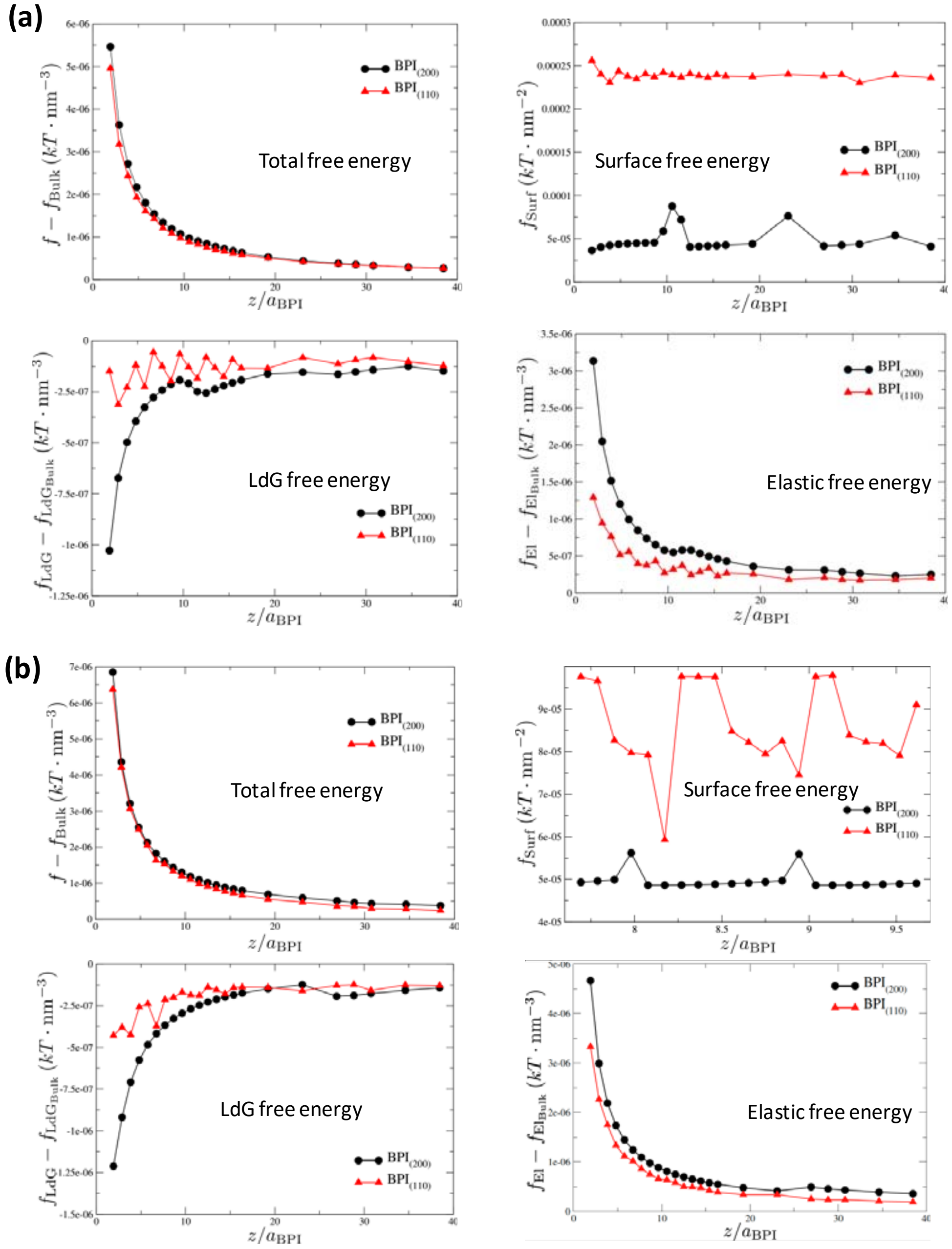

Figure S6 Components of the free energies of BPI films confined between surfaces mediating (a) degenerate and (b) uniform planar anchoring with W = 7x10^{-4} J/m^2, respectively. P = 500 nm.

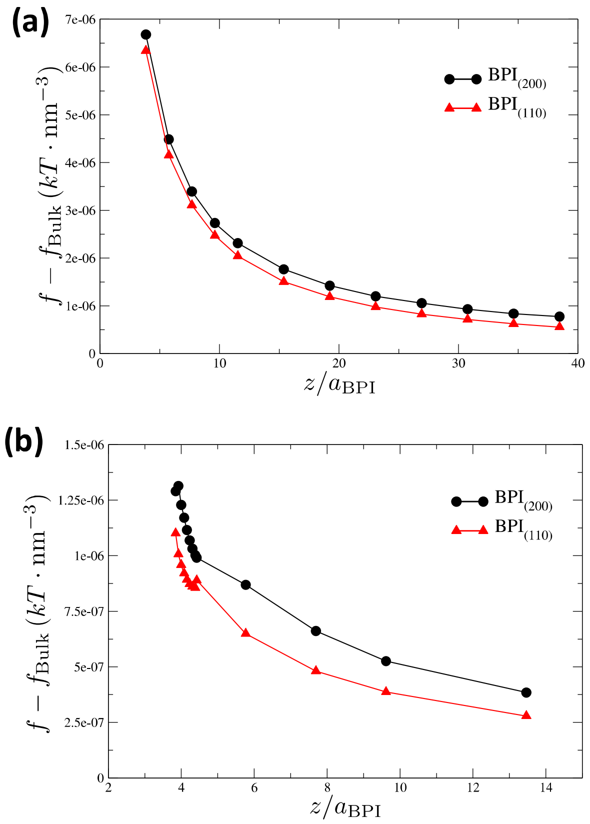

Figure S7 Free energies of BPI films confined between surfaces mediating (a) homeotropic with W = 10^{-3} J/m^2, (b) uniform planar anchoring with W = 10^{-5} J/m^2, respectively. Free energies of BPI oriented (black) (100) and (red) (110) planes parallel to the contacting surfaces. P = 500 nm.

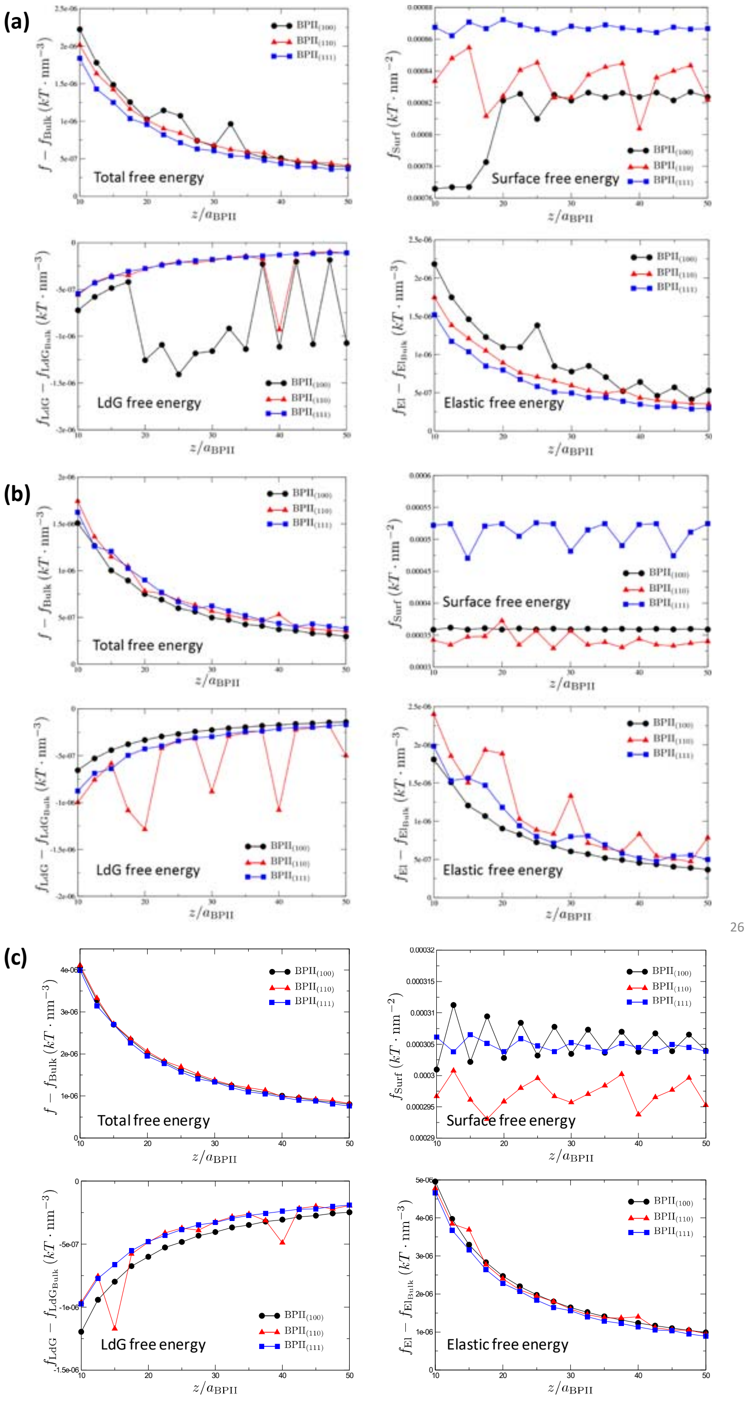

Figure S8 Components of free energies of BPII films confined between surfaces mediating (a) degenerate planar, (b) uniform planar, and (c) homeotropic anchoring. Free energies of BPII oriented (black) (100), (red) (110) and (blue) (111) planes parallel to the contacting surfaces. P = 344 nm in all simulations. W is 7x10^{-4} J/m^2 in (a, b) and 10^{-3} J/m^2 in (c).

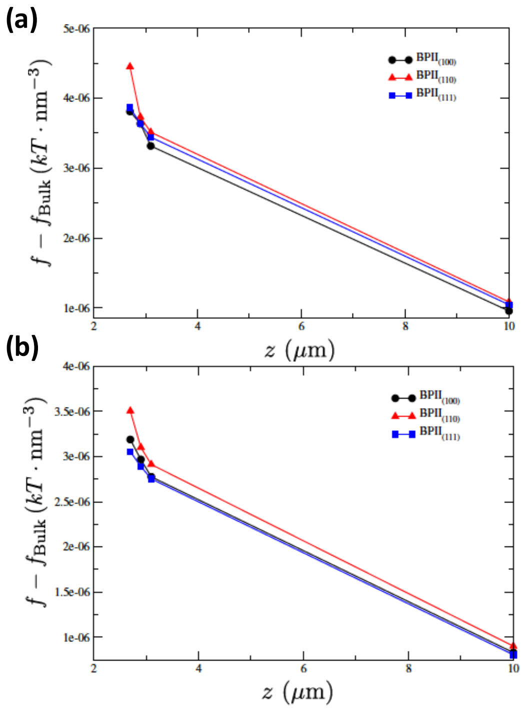

Figure S9 Free energies of BPII films confined between surfaces mediating (a) uniform planar, and (b) degenerate planar anchoring. Free energies of BPII oriented (black) (100), (red) (110) and (blue) (111) planes parallel to the contacting surfaces. P = 344 nm in all simulations. W is 10^{-3} J/m^2 in (a) and 10^{-5} J/m^2 in (b).

References

1. T. H. Blumel and H. Stegemeyer, *Liquid Crystals*, 1988, **2**, 195-201.
2. A. I. Feldman, P. P. Crooker and L. M. Goh, *Physical Review A*, 1987, **35**, 842-846.