

Supporting Information

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SI Text

An expanded explanation of blue phases and additional relevant references are provided. Main advantages of using blue phases for 3D self-assembly, only listed in the manuscript, are explained here.

Textures of Blue Phase I and Blue Phase II. Three thermodynamically stable blue phases (BP) I, II, and III occur in a temperature range between the isotropic and cholesteric phases of highly chiral liquid crystals (1). BP III has an amorphous structure, whereas BP I and BP II both exhibit cubic orientational order, with space groups $O^8-(I4_132)$ and $O^2(P4_132)$. The unit cell sizes of blue phases are typically in visible range (a few 100 nm), therefore being attractive for use as modulators, photonic crystals or tunable lasers (2–4). Recent discoveries of molecular mixtures with a broad blue phase range (5) and development of polymer stabilized blue phases (6) have opened gates to electro-optical applications. Indeed, liquid crystal (LC) display based on blue phases with a superior 240 Hz refresh rate have been demonstrated recently.*

The texture of the blue phases is based upon preferred molecular orientation forming cylindrical regions of local double twist, where the molecules rotate away from the axis to form a helical vortex that represents the best local packing of chiral molecules. These double-twist cylinders are then assembled into a space filling, periodic, three-dimensional array. For topological reasons the molecular orientation cannot be extended smoothly throughout the spaces between the double-twist cylinders so that a periodic lattice of defect lines, known as disclinations, is necessarily formed. The stability of the blue phases is because of a delicate balance between the free energy savings provided by the double-twist regions and the cost of the topologically required disclination lines

Textures of BP I and II are presented in Fig. S1. Note, the stacking of double-twist cylinders.

Advantages of Using Blue Phases for 3D Self-Assembly. Strong potentials and robustness. The main advantage of using cholesteric blue phases is that despite being liquid, they possess the 3D crystalline symmetry of the underlying molecular orientational ordering, which effectively produces periodic 3D trapping potential for colloidal particles. The binding energy of particles to the trapping sites can be as large as a few 100 $k_B T$ for 100 nm particles, which

is one (two) orders of magnitude larger as compared to interparticle potentials of water-based or charge-based colloids. Having binding energies much larger than $k_B T$ assures robustness of the material with respect to thermal fluctuations and also other external perturbations. We note that, Kikuchi et al have dispersed polymers in blue phases (6); Adding particles to blue phases should require generalization of their process.

Highly regular large scale trapping potentials. The size of blue phase monodomains can easily be approximately 100 μm . For example, the recent demonstration of blue phase-based television by Samsung Electronics* indicated that blue phases can be controlled at macroscopic dimensions implying that highly regular trapping potentials for colloidal particles can be assured even over macroscopic length scales.

Simple control of the colloidal crystal via LC restructuring. Using a liquid crystalline template for particle assembly makes blue phase colloidal crystals highly responsive to external stimuli. The colloidal particles are effectively pinned to the internal structure of the blue phase; therefore by changing the blue phase structure (unit cell) the colloidal crystal also changes. Blue phases can be well controlled by temperature (1) and external electric field (7). By slowly changing the temperature or external electric field, the size of the blue phase unit cell changes smoothly, which allows for fine-tuning of colloidal crystal lattice constants. In contrast, by making larger changes in temperature or using larger electric fields, structural transitions between various distinct blue phase structures can be triggered (mesophases BP I–III, field induced phases), which makes possible full restructuring of the colloidal crystal.

Possible coimplementation of blue phase-based self-assembly to nonliquid crystal-based assembly techniques. For material handling, dispersions of blue phase colloids are, except for the internal molecular orientational order, similar to classical water-based or oil-based colloids. Concepts and technologies developed for these “isotropic” colloids can therefore be relatively simply transferred to blue phase colloidal crystals. We list only few attractive concepts: manipulation by thermophoresis (8), diffusophoresis by solute contrasts (9), and patterning of colloidal structures by lift up soft lithography (10).

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*In May 2008 Samsung Electronics announced that it has developed the world's first Blue Phase LCD panel which can be operated at an unprecedented refresh rate of 240 Hz. Samsung unveiled a 15 in. prototype model of its Blue Phase LCD panel at the Society for Information Display 2008 International Symposium, Seminar, and Exhibition, which was held in Los Angeles from May 18 to 23, 2008.

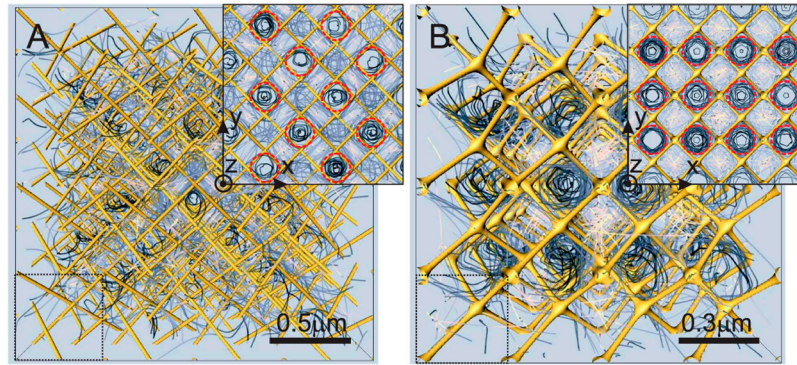


Fig. S1. BP I (A) and II (B) standing for blue phase $4 \times 4 \times 4$ unit cells are presented in 3D view; insets show two-dimensional projections of the structures. Single unit cell sizes are indicated by dotted squares. The lattice of disclination lines is presented in yellow as isosurface of nematic degree of order $S = 0.2$. Gray lines visualize the average orientation of the molecules—the director. In the insets, note the stacked helical double-twist cylinders (encircled in red). Stacking of double-twist cylinders is equivalent in xz and yz plane.