

Self assembly and self-organization of supermolecular liquid
crystals in the context of anisotropic building blocks

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I. Introduction

A. Liquid crystals and their rich phases

a. Liquid Crystals

Liquid crystals (LCs) are a state of matter that have properties between those of a conventional liquid and those of a solid crystal¹, e.g. an LC may flow like a liquid, but its molecules may be oriented in a crystal-like way. Within a certain domain, the molecules are well ordered. Traditionally, most liquid crystals have been designed to be either low molar weight for displays or high molecular weight for prototypical high yield strength polymers².

b. Liquid crystal phases

The type of their ordering can characterize the various LC phases (also known as mesophases). These orders include: Positional order (whether molecules are arranged in any sort of ordered lattice); Orientational order (whether molecules are mostly pointing in the same direction); Short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions) order.

At high enough temperatures, most thermotropic LCs will have an isotropic phase because of the fact that heating will eventually drive them into a conventional liquid

phase characterized by random and isotropic molecular ordering (little to no long-range order), and fluid-like flow behavior. Under other conditions, e.g. by lowering the temperature, an LC might show one or more phases with anisotropic orientational structure and short-range orientational order.

There are many different types of LC phases, which can be distinguished by their different optical properties³. Here are the three most commonly studied LC phases in supermolecular materials.

1. Nematic phase

One of the most commonly seen LC phases is the nematic phase. In a nematic phase, the calamitic or rod-shaped organic molecules have no positional order, but they self-align to have long-range directional order with their long axes roughly parallel⁴. Thus, the molecules are free to flow and their center of mass (CM) positions are randomly distributed as in a liquid, but still they maintain their long-range directional order. Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent. Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field.

2. Smectic phases

Smectic phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another in a manner similar to that of soap⁵. The smectics are thus positionally ordered along one direction. In the Smectic A phase, the molecules are oriented along the layer normal, while in the Smectic C phase they are tilted away from the layer normal. There are many different smectic phases, all characterized by different types and degrees of positional and orientation order.

3. Chiral phases

Chiral nematic phase exhibits chirality (handedness)⁶. Only chiral molecules (i.e., those that lack inversion symmetry) can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director. The finite twist angle between adjacent molecules is due to their asymmetric packing, which can result in longer-range chiral order.

B. Pattern formation in liquid crystals

One of the most important signatures of self-organization is spontaneous pattern formation. Anisotropy of liquid crystals is a unique property not observed in other fluids. This anisotropy makes liquid crystal phases be accompanied by potential novel pattern formation. Many but not all features include: 1. Injection of a flux of a liquid crystal between two close parallel plates (viscous fingering), causes orientation of the molecules to couple with the flow, with the resulting emergence of dendritic patterns⁷. 2. The equilibrium shape at the coexistence temperature in the interfacial energy (surface tension) between different liquid crystal phases, and when temperature is

changed one of the phases grows, forming different morphologies depending on the temperature change⁸. 3. Anisotropy in thermal conductivity favors growth in specific directions, which has also an effect on the final shape⁹. 4. Polarization-modulated smectic liquid crystal phases¹⁰, in which local splay prevails in the form of periodic supermolecular-scale polarization modulation stripes coupled to layer undulation waves.

C. Supermolecule

A supramolecular assembly or "supermolecule" is a well-defined complex of molecules held together by noncovalent bonds¹¹. The very engines of living systems are based on supermolecular and supramolecular self-organizing and self-assembling systems of discrete structure and topology¹².

II. Self-organization and phase formations of supermolecular liquid crystals with shape anisotropic building blocks

Through self-assembly and self-organization processes, liquid crystalline phases have opened up new perspectives in materials science towards the design and engineering of supramolecular materials¹². The self-organization in two and three-dimensional space offered by the liquid crystalline medium is an ideal vehicle to explore and control the organization of matter on the nanometer to the micrometer scale which are key to the emerging development of nanotechnology.

A. The effects of anisotropy at the level of mesogenic group

Mesogenic group is a part of a molecule or macromolecule endowed with sufficient anisotropy in both attractive and repulsive forces to contribute to liquid crystal mesophases formation.¹³

The way supermolecules self-organize is dependent on simple structural features: The density of the mesogenic units attached to the periphery of the central scaffold, their orientation of attachment, and the degree to which they are decoupled from the scaffold, e.g. the density of mesogenic groups attached to the periphery can effectively change the overall gross shape of the structure of the supermolecule from being rod-like, to disc-like. The structure of the systems at a molecular level can be considered as being deformable, where each type of molecular shape will support different types of self-organized mesophase structure. For supermolecular materials, rod-like systems will support the formation of calamitic mesophases, disc-like systems tend to support columnar mesophases, and spherulitic systems form cubic phases, as shown below¹⁴:

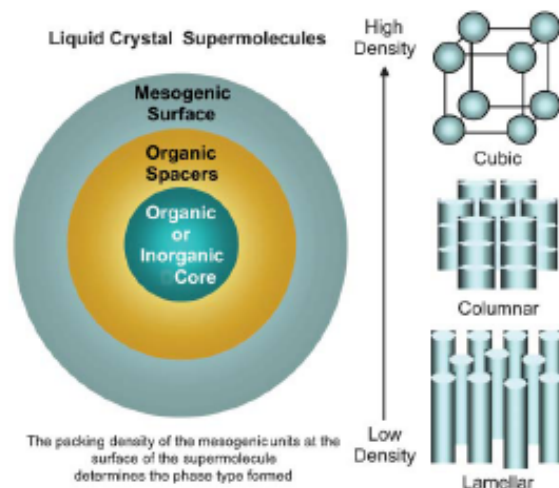


Fig. 1 (Snapshot from reference 14) Effect of the number density of mesogens on the surface of the supermolecular structure on the formation of various mesophases.

Though extensive research studies into the effects that the type (rod-like, disc-like or spherulitic) of mesogenic group attached to the central scaffold has on mesophase formation are still missing, it is clear for rod-like shaped mesogenic groups that the orientation of the attachment can markedly influence the type of mesophase formed and polymorphism of any smectic phases formed.

Apart from number density and orientation of attachment, the degree to which the mesogenic units are decoupled from the central structure plays a major role. The shorter the linking unit is, the more likely the material will act as single supermolecular entity, whereas the longer the spacer the more likely it is that the properties of the individual mesogenic groups will be dominating the overall properties of the material.

B. The effects of anisotropy at the level of particles

New approaches to particle synthesis have led to an unprecedented diverse spectrum of particle anisotropy¹⁵ (Shown below in Fig. 2)

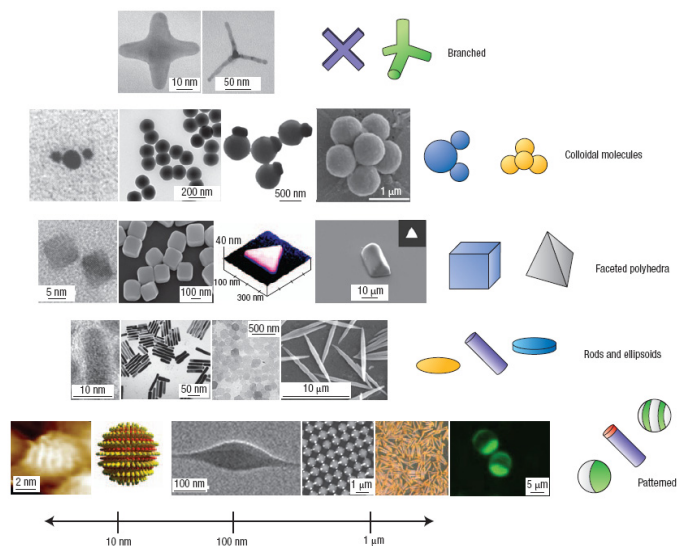


Fig. 2 (Snapshot from reference 15) Representative examples of recently synthesized anisotropic particle building blocks. The particles are classified in rows by anisotropy type and increase in size from left to right according to the approximate scale at the bottom. Image Copyright, as appropriate, AAAS, ACS, RSC, Wiley-VCH.

Colloidal suspensions of spherical or anisometric particles and their mixtures provide a vast variety of order-disorder phase transitions. A classical example is the seminal work of L. Onsager on the liquid crystal behavior of anisotropic rod-like colloids.¹⁶ The well-defined particle shapes and the possibility to control the interparticle interactions render colloidal suspensions the mesoscale analog systems for the study of supermolecular liquid crystal phase transitions.

a. One component anisotropic building colloids

Anisometric nanocolloids are similar to molecular liquid-crystal mesogens. In one study, the quality of the nematic alignment factor in sedimented particles was comparable to typical qualities of liquid-crystalline polymers¹⁷. Simulations have extended the possible analogy into new realms, e.g. nanocolloidal cubes are predicted to form a cubatic phase that has liquid crystalline character¹⁸.

b. Binary mixtures of anisotropic building colloids

Studies have been carried out on the spontaneous self organization and on the phase decomposition of mixtures of rod-like and spherical particles¹⁹. Apart from the isotropic phase, these mixtures may exhibit uniform nematic phases and lamellar phases or, depending on the relative concentration of the two species, they may demix into phases of different symmetry. For example, a broad isotropic-nematic coexistence region has been observed²⁰ at low temperatures in a temperature-concentration phase diagram of a mixture of rods (low molecular mass LC) and larger particles (silicon oil). A recent theoretical study²¹ for binary mixtures with a model of shape anisometric particles embedded in a cubic lattice obtained following findings:

1. Rod-sphere mixtures

For the mixtures of rod-like with spherical particles, it is found that thermodynamically stable isotropic, nematic and lamellar phases as well as triphasic coexistence between these phases and regions of biphasic coexistence of all possible combinations of the three phases. The lamellae form a succession of rod-rich and sphere-rich layers. We have also found that the presence of soft shell repulsions between the rods and the spheres tends to destabilize the lamellar phase relative to the nematic.

2. Plate-sphere mixtures

For mixtures of plate-like with spherical particles, isotropic, nematic and columnar phases are found. The presence of soft shell repulsions between the rods and the spheres tends to produce two different isotropic phases in coexistence over a relatively wide range of compositions.

3. Rod-plate mixtures

More phases are found in mixtures of plate-like with rod-like particles. The thermodynamically stable phases include an isotropic, a columnar and two types of uniaxial nematic phases. Triphasic and biphasic coexistence is obtained for several combinations of these four phases.

III. Self-organization and Pattern Formation of anisotropic building blocks

Self-organization drives and is driven by the spontaneous formation of supramolecular entities that remain associated by non-covalent interactions.

An example follows from a recent Monte Carlo simulation²² of the phase behavior of core-shell Janus particles assuming selectively repulsive interactions to mimic the amphiphilicity (see Fig. 3 below) of the particles.

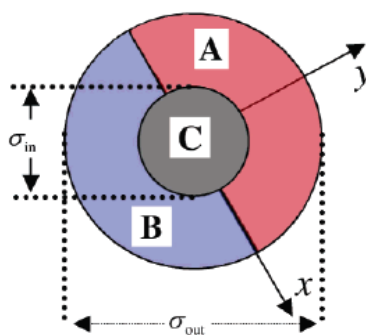


Fig. 3 (Snapshot from reference 22) Model disklike Janus particle used in the simulations. It consists of the internal hard core (C) of diameter σ_{in} and a soft corona with outer diameter σ_{out} divided into two sections (A and B) of opposite philicity.

Besides the isotropic phase and depending upon the coronal thickness, the simulated systems self-organize into a number of two-dimensional mesophases accompanied by

spontaneous pattern formation, indicating the development of strong orientation-position correlations.

Inspection of the snapshots shown on the left part of Fig. 4 gives a visual impression of the nature of the molecular organization in the low and high-pressure phases for different particle anisotropy cases.

For the thin corona case, the low-pressure phase is apparently disordered but with the particles tending to form large aggregates. The high-pressure phase, on the other hand, shows zipper-like stripes that break at irregular distances into orthogonal sections.

For the thick corona case, two phases were found upon compression, a disordered isotropic phase, through a rather strong first-order phase transition, to a crystalline phase. Molecular organization in both phases differs qualitatively from the previously studied phases. In the isotropic phase, the particles show a clear tendency to self-assemble in chains, which resembles a polymer network. The large corona thickness makes it possible for the homophilic coronal parts of more than two particles to overlap at the same time allowing for intersections, branching of molecular chains, and leading to formation of a large variety of linear, branched, and closed chain configurations. Under high pressure, triplets of particles self-assemble into aggregates with the hard cores forming the three apexes of an equilateral triangle and with the coronal sectors of the same philicity pointing to the interior of the triangle (see Fig. 4 (Right) c). And these triplets self-organize into a superstructure with the internal hard cores located on a Kagome-like lattice.

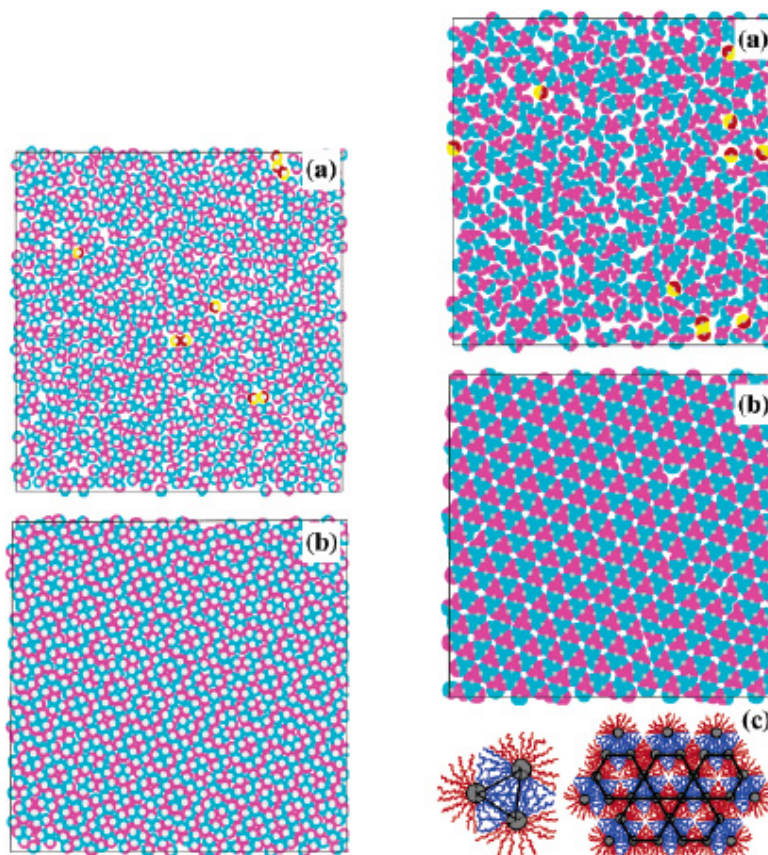


Fig. 4 (Snapshot from reference 22) Representative phases corresponding to cases with different particle structure configuration: A thin(left) and B thick (right) corona.

Left: Typical snapshots of the two different phases exhibited by system A.

(a) Isotropic phase at low pressure. (b) Crystal phase at high pressure.

Right: Typical snapshots of the low (a) and high (b) pressure phases exhibited by the system B, respectively.

(c) Schematic representation of a three-particle aggregate (lower left) and its supramolecular organization in a Kagome lattice (lower right).

IV. Conclusions

In summary, we have reviewed some recent work on self-assembly and self-organization of supermolecular liquid crystals in the context of anisotropic building blocks. These novel anisotropic units, either on the level of mesogenic group or particles, are expected to become the building blocks of novel materials based on successful self-assembled structures desired. A variety of liquid crystal phases are observed accompanied by novel pattern formation in such systems. In general, it is shown that anisotropic building blocks have the potential to serve as a new route to general materials design strategy.

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