

Self-Assembly of Phase-Segregated Liquid Crystal Structures

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Additional functionality can be incorporated into liquid crystalline materials by using phase segregation and self-assembly. Intermolecular interactions such as hydrogen bonding and ionic interactions play key roles in the formation of these complex structures. One-, two-, and three-dimensional phase-segregated structures on various scales of length are formed by self-assembly of a variety of partially incompatible molecules. Such structures can enhance anisotropic properties such as ionic conductivity.

Molecules in the liquid crystalline (LC) state, although still mobile, have an orientational ordering that depends on external conditions, such as temperature or electric fields (1, 2). The best known example would be the thermotropic LC materials, which exhibit different phases as a function of temperature, that are used in displays (3). In contrast to these high-tech materials, biological self-assembled systems consist of a variety of discrete molecules forming heterogeneous and hierarchical structures (structures within structures) on various scales of length ranging from the nanometer to the micrometer scale. For example, lipids exhibit lyotropic LC states in which phase formation depends on solution concentration (4). Biological cell wall membranes are formed through self-assembly of lipids with other biomolecules such as proteins and steroids.

Self-Assembled and Phase-Segregated Liquid Crystals

Although the intrinsic ordering within a LC material can be controlled by external parameters, the ordering can also be controlled internally through weak interactions to create more complex structures that add functionality to the material. One approach is to obtain self-assembled structures from a variety of different molecules (2, 5–10). Another is to form phase-segregated structures of “block” molecules of longer polymers and smaller molecules on the nanometer and micrometer scale (2, 10–12). The control of intermolecular interactions (noncovalent interactions) within these structures is critical because several competing effects are at work.

In the formation of the self-assembled LC structures, specific intermolecular interactions such as hydrogen bonding and ionic interactions play key roles. A notable example is the formation of supramolecular liquid crystals (5–9). In the case of these materials,

well-defined structures such as rods and disks are made through self-assembly of two or more complementary molecular components by hydrogen bonding. For example, benzoic acids and pyridines form supramolecular rod-like complexes exhibiting thermally stable nematic and smectic (layered) LC phases (5, 6, 9). Moreover, identical molecules self-assemble into unconventional LC complexes (13, 14). Studies of these materials have initiated and stimulated the development of supramolecular polymers (15, 16).

One advantage of these supramolecular materials is that they can respond to external stimuli and to different environments by changing their self-assembled structures (13) and by the dissociation and association of noncovalent interactions (5, 9). For example, a thermotropic folic acid derivative exhibits a change from smectic to hexagonal columnar phases by the addition of alkali metal salts (Fig. 1). In this phase change, the hydrogen-bonded pattern is changed from ribbon to disk because ion-dipolar interactions between the added sodium ion and the disklike assemblies stabilize the columnar LC structures. These LC phases are stable up to nearly 250°C. Changes in pH or ionic strength in the hydrogen-bonded systems may also induce or destroy ordering, which can be used as a readout in sensor application. These ion-induced LC structural changes are related to the ion-induced morphological changes of block copolymer aggregates (17).

The formation of the phase-segregated LC structures is similar to the case for block copolymers; molecules having two or more incompatible parts must microphase separate (18, 19). Conventional phase-segregated liquid crystals are lyotropic low-molecular-weight (LMW) molecules (4), wherein LMW amphiphilic molecules and water form complex segregated structures of hydrophilic and hydrophobic parts on the nanometer scale (molecular length scale <10 nm). Layered, columnar, and cubic structures are exhibited by these amphiphilic molecules (4). Such morphological features are similar to those of the segregated structures of block polymers

with a greater length (>10 nm) (18, 19). Recently, new LC materials exhibiting phase-segregated structures have been reported (10–12, 19–24). For example, LC dendrimers exhibit phase segregation of their core parts, such as siloxane cages and C₆₀ and mesogenic rodlike parts at their periphery (20, 21). These materials are new LC inorganic–organic hybrids. For side-chain LC block copolymers, they show temperature-dependent phase-segregated structures, which can switch charge conductivities or optical properties (22–24).

Very recently, both self-assembly and phase segregation have been combined in the making of liquid crystals (25–40). This new methodology has been developed to fabricate functional molecular materials and devices. Electrical, ionic, and optical properties as well as bioactive properties, which are quite different from those of conventional materials, are expected to be exhibited in these self-assembled materials. Such new functional complex structures with liquid crystals are created from several partially incompatible molecules including functional moieties.

Phase-Segregated Structures Transporting Charges and Ions

Columnar structures can facilitate the transport of charged species in soft materials (41, 42). Phase-segregated LC structures on the nanometer scale can be used in their syntheses. Gin *et al.* have prepared electroactive materials by columnar self-assembly of an amphiphilic polymerizable molecule, water, and a water-soluble precursor of a conductive polymer (25), poly(*p*-phenylene vinylene) (PPV). A stable hexagonal arrangement was created through the self-assembly, as shown in Fig. 2. In this structure, PPV is one-dimensionally aligned in the hexagonal matrix on the nanometer scale. After polymerization of the amphiphilic molecules and heat treatment of the precursor, conductive nanocomposites were obtained. These segregated structures enhance the photophysical properties of the PPV.

Thermotropic columnar liquid crystals such as discotic triphenylenes have been employed for one-dimensional (1D) photoconductors (41, 42). The approaches to self-assembly (43) and phase segregation (26) in these discotic materials have enhanced their photofunctionalities. For example, the charge mobility of a triphenylene molecule became

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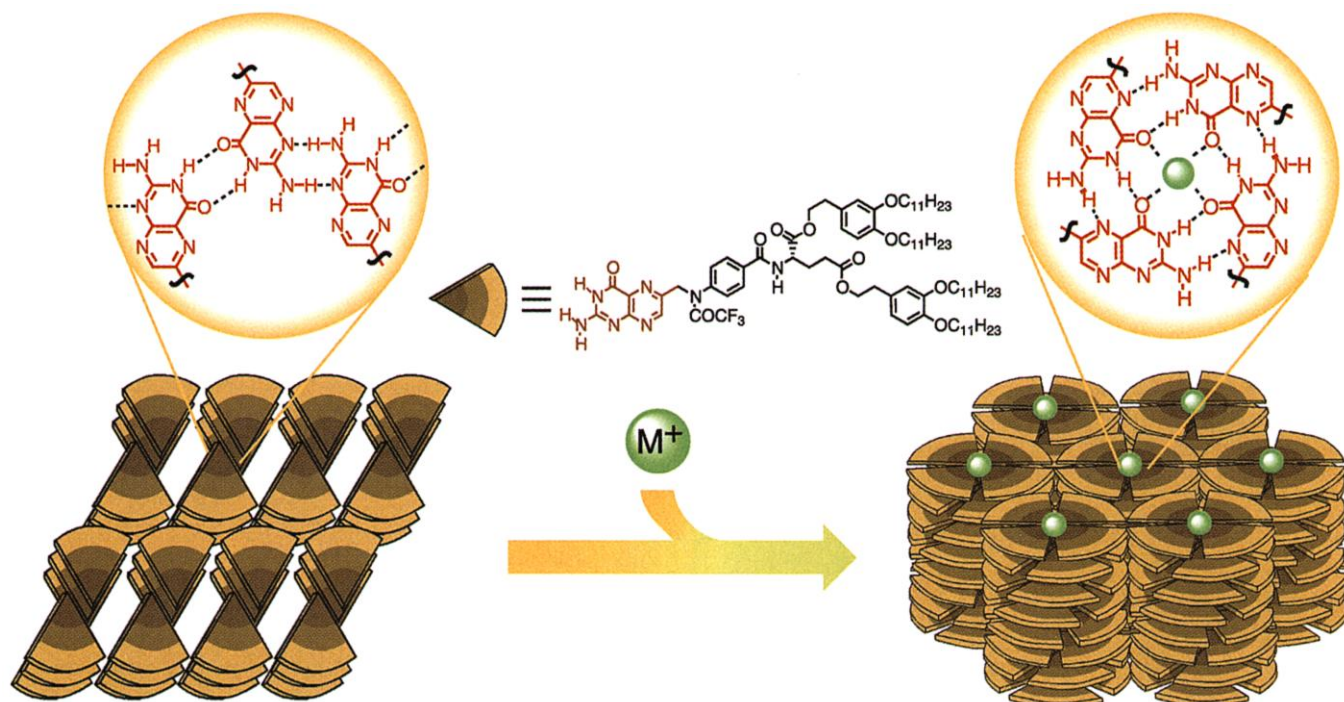


Fig. 1. Ion-responsive self-assembled liquid crystals. Ribbonlike structures of a folic acid derivative and their structural change to the disklike tetramers by the addition of metal ions (M^+) are shown.

three times faster by forming phase-segregated structures with hydrogen-bonded fibrous aggregates (26).

Self-assembly of the hexagonal phases of ions and organic molecules can be used to create 1D ion conductors. When lithium salts and block molecules containing poly(ethylene oxide) (PEO) moieties and long hydrocarbon chains are mixed, hexagonal columnar LC phases formed through nanometer-scale segregation are obtained (27). The PEO moieties are compatible with the lithium ions and form ion-transporting channels in the center of the column, and the hydrocarbon moieties function as ion insulators. However, long-range ion-conducting paths that are longer than millimeters, which may be useful for wider applications, have not yet been formed for columnar structures.

2D conductive materials can also be designed, because ions are incorporated into the self-assembled layered structures (28–30), as shown in Fig. 3. Long-range ion-conducting paths are easily formed for smectic materials, which tend to form homeotropic monodomains. For example, block rod-coil-rod molecules, in which the rod is an aromatic mesogen and the coil is a PEO moiety, are used for the layered assembly with lithium salts, leading to the induction of the smectic LC structures (29). The lithium salts are incorporated into the 2D PEO layer of nanometer-scale thickness in cm-scale length. In these smectic phases forming phase-segregated structures, efficient ion transportation along the smectic layer is observed. Highly anisotropic ion

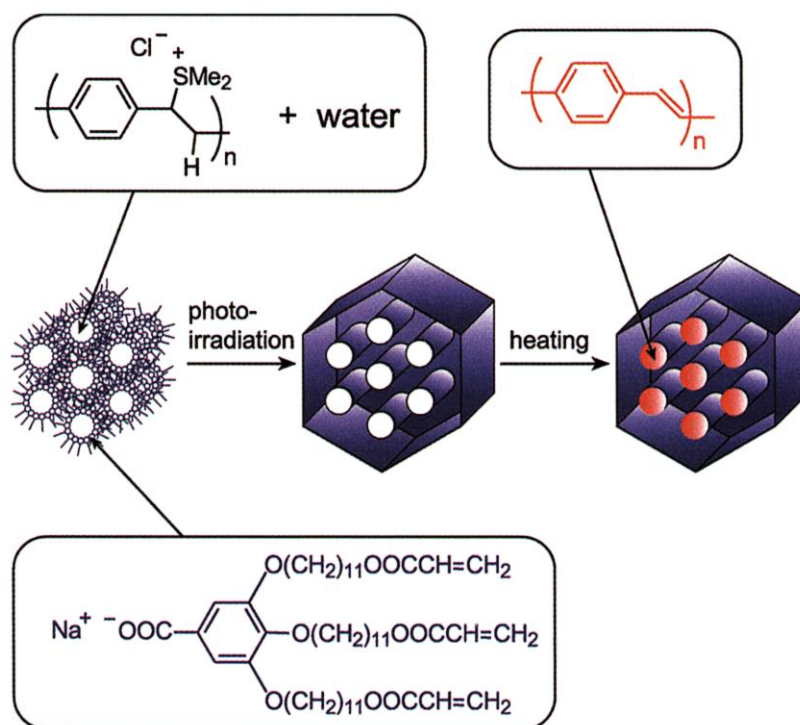


Fig. 2. Nanometer-scale 1D phase segregation. Self-assembly and fixation of a hexagonal columnar phase containing a conductive polymer are shown.

conduction in LC materials will be useful for the design of new battery materials and ionic devices.

The design of the anisotropic ion-active structures can be extended to the organization of ionic liquids (Fig. 3) (30). Ionic liquids have recently attracted much attention be-

cause of their great potentials as electrochemical devices (44) and as reaction solvents that avoid complex separation problems (45). The 2D nanometer-scale organization through the self-assembly of conventional ionic liquids and hydroxyl-terminated LC molecules was achieved by Kato *et al.* (30). The interactions

between the hydroxyl moieties and the ionic liquids stabilize the layered LC assembly. The anisotropic ionic conductivities have been obtained for these materials because they exhibit stable monodomains between electrodes. In the smectic phases, the ion conductivities parallel to the smectic layer are between 100 and 1000 times higher than are those perpendicular to it.

Fig. 3. Nanometer-scale 2D phase-segregation in smectic phases consisting of lithium salts and rod-coil-rod molecules containing PEO moieties or conventional ionic liquids and hydroxyl-terminated rodlike molecules.

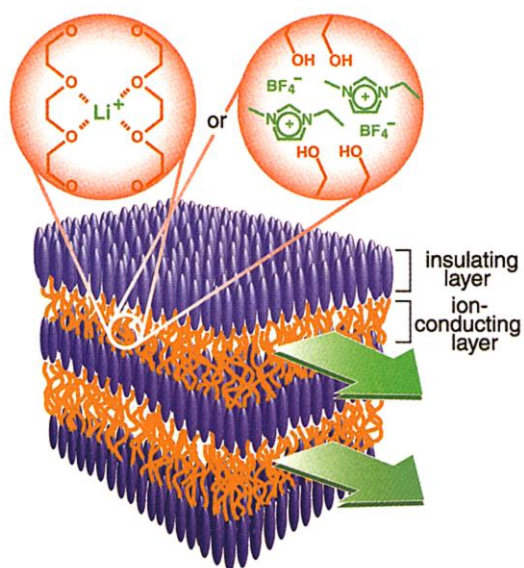
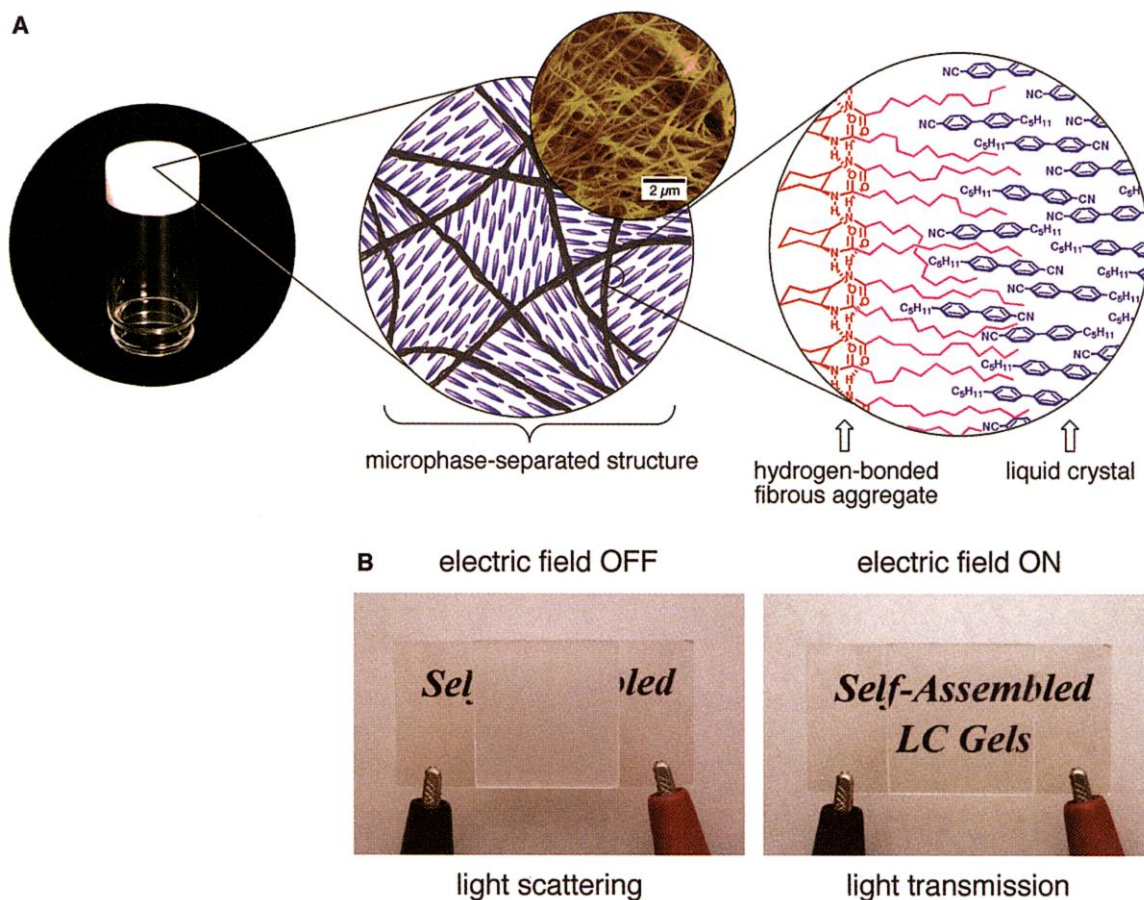


Fig. 4. Micrometer-scale phase segregation of liquid-crystalline physical gels. (A) Hierarchical structures consisting of self-assembled fibers and conventional rodlike liquid crystals. (B) Left, light-scattering state (with the electric field off); right, light-transmission state (with the electric field on).



to 70 weight percent (wt %)]. These phase-segregated structures induce light-scattering milky-white states, which can be switched to transparent states by the application of electric fields. Another group is LC chemical gels (49, 50), which are obtained by the polymerization of solutes in nematic, cholesteric, or smectic liquid crystals. In contrast to PDLCs, LC chemical gels contain smaller amounts (normally less than 10 wt %) of polymers. The dispersion of polymer networks in the ferroelectric liquid crystals improves mechanical strength (shock resistance) and induces orientation stability (49–51).

Recently, physical gelation of organic solvents by the fibrous aggregation of small molecules (gelators) has attracted much attention (52). Such gelators have been found to gel thermotropic liquid crystals (26, 31–34). Self-assembly of these two discrete components—hydrogen-bonded gelators and conventional rodlike LC molecules—results in the fabrication of LC physical gels, leading to a micrometer-scale phase segregation, as shown in Fig. 4A. The fibrous network aggregates in the liquid crystals, causing the formation of the anisotropic soft solids (Fig. 4A, left). These physical gels exhibiting phase-segregated structures are easily obtained through the fibrous self-assembly of gelators in liquid crystals after the mixtures

are cooled from the isotropic liquids. They thermoreversibly exhibit the liquid (solution) and gel states due to the dissociation and association of hydrogen bonding.

The LC physical gels show faster electro-optical responses in twisted nematic (TN) cells (32). The TN mode is now used as a standard for information displays (3). In TN cells, the segregated structures containing less than 0.5 wt % of gelators, based on weight of the amino acids, can lead to a faster switching of the molecules due to the presence of electric fields. The balance of the interactions of the LC molecules with the electrode surfaces and fibrous aggregates plays a key role in such molecular dynamic behavior. The simple self-assembly processes enable us to easily tune the phase-segregated morphologies such as the diameters, lengths, and densities of fibers, in addition to the randomness or order of the fibers. This leads to faster responses, lower driving voltage, and higher contrast with an even smaller amount of gelators.

When the gels contain more than 1.0 wt % of gelator, the phase-separated structures cannot be used for TN cells, because of light scattering. To make appropriate gels, the light-scattering and light-transmission states are switched on and off by electric fields between transparent electrodes (Fig. 4B) (33). The light scattering of these gels is efficient because the appropriate size and shape of "fibers" are dispersed randomly (Fig. 4B, left). The micrometer-scale phase-segregation of the self-assembled fibers (solid state) and the nematic liquid crystals (LC state) seems to show advantages for light-scattering electro-optical materials. These approaches may lead to the fabrication of thin, flexible paperlike displays based on liquid crystals. Phase-segregation of liquid crystals with organic particles (53, 54) and dendrimers (55) has also been reported. We examined the rela-

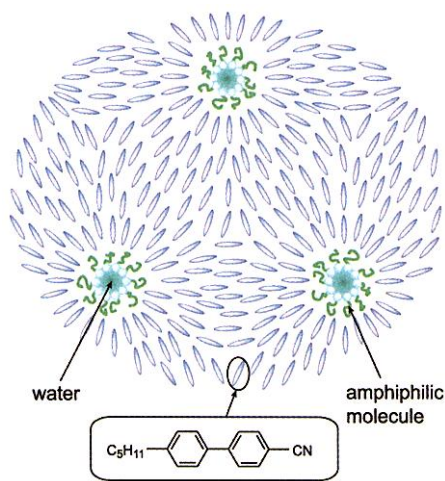


Fig. 5. Nanometer-scale 3D phase segregation of inverse micelles and conventional rodlike liquid crystals. A transparent nematic phase is shown.

tion between phase-segregated morphologies and light-scattering electro-optical properties.

Anisotropically oriented microphase-separated structures are obtained when the self-assembly of a gelator occurs in liquid crystals (34). The self-assembled fibers are aligned parallel to the smectic layer and maintain a uniform distance of 10 μm . The liquid crystals could thus act as templates for the 1D alignment of functional molecules such as electroactive molecules.

When the inverse micelles consisting of water and LMW amphiphilic molecules are introduced into conventional nematic liquid crystals, a new type of complex fluids that form nanophase-segregated structures is obtained, as shown in Fig. 5 (35). Yamamoto and Tanaka have prepared a transparent nematic phase by using such a nanometer-scale segregation. The optically isotropic structures are obtained even though the local nematic order is maintained because nanometer-scale droplets interact with the rodlike molecules, resulting in the disturbance of the long-range nematic order. Moreover, the distance between the micelles is much shorter than the wavelength of light. These materials are expected to exhibit unique optical and rheological properties.

Phase-Segregated Structures with a Bioactive Function

Complex LC structures can be applied not only in high-tech fields but also in biorelated fields, because lyotropic phases are often seen in biomolecular systems. For example, Safinya *et al.* reported that ionic interactions between DNA and cationic liposomes direct self-assembly of lyotropic LC lamellar structures on the nanometer scale (36, 37). These DNA containers have potential application in gene therapy because the complexes can bring DNA into the cell through fusion with the cell mem-

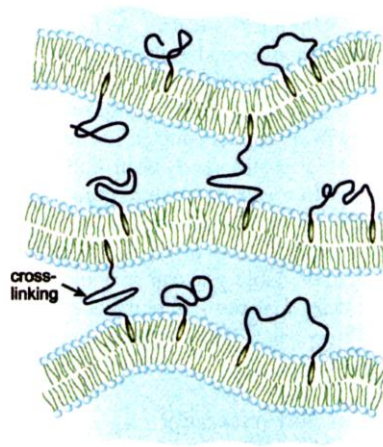


Fig. 6. Lamellar biogels showing self-assembly of a lipid and an amphiphilic PEO-based triblock copolymer. Physical cross-linking formed between the membranes is shown.

brane. The mixtures of lipids and a small amount of aliphatic-PEO-aliphatic triblock copolymers form LC physical hydrogels (38, 39). The triblock copolymer functions as a gelator that bridges fluid bilayers (Fig. 6). These materials maintain fluid states even though they show mechanical stability and elastic properties. They can be used as bioactive membranes, which can be used for drug delivery or tissue-healing applications. Self-assembled lipid bilayers can also function as templates for the formation of nanometer-scale conduits and networks (40). In these materials, the photopolymerization of a dimethacrylated PEO in aqueous solution confined by the lipid bilayer yields cross-linked nanotubes, which can immobilize proteins and cells for nanometer-scale electron modulator and biosensors.

Moreover, biomolecules such as sugars (2), poly(amino acid)s (56), vitamins (13), and cholesterol (57) show thermotropic and lyotropic LC phases. Tirrell *et al.* have shown that monodisperse poly(benzyl glutamate)s prepared by bacterial syntheses exhibit smectic ordering in solution and films (56). These materials can be used for diffraction grating and membranes with controlled permeability. The introduction of complex and hierarchical structures to these biomolecular materials may lead to the induction of bioactive function and the fabrication of new stimuli-responsive materials.

Conclusion

The creation of complex phase-segregated structures with liquid crystals may widen the applicability of liquid crystals in high-tech and biorelated fields. Phase-segregated structures of various scales of length (1 to 1000 nm) and of various types of ordered structures can be simply achieved through self-assembly of a variety of interacting molecular components if their chemical structures are well designed. Moreover, anisotropy and molecular dynamics can be introduced into these materials, forming LC states. The creation of more complex hierarchical structures with liquid crystals leads to the induction of dynamically functional properties on the molecular level, such as sensing and transportation of electrons, ions, and molecules, as well as templating.

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VIEWPOINT

Self-Assembly at All Scales

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Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembling processes are common throughout nature and technology. They involve components from the molecular (crystals) to the planetary (weather systems) scale and many different kinds of interactions. The concept of self-assembly is used increasingly in many disciplines, with a different flavor and emphasis in each.

There are several reasons for interest in self-assembly (1, 2). First, humans are attracted by the appearance of order from disorder. Second, living cells self-assemble, and understanding life will therefore require understanding self-assembly. The cell also offers countless examples of functional self-assembly that stimulate the design of non-living systems. Third, self-assembly is one of the few practical strategies for making ensembles of nanostructures. It will therefore be an essential part of nanotechnology. Fourth, manufacturing and robotics will benefit from applications of self-assembly. Fifth, self-assembly is common to many dynamic, multicomponent systems, from smart materials and self-healing structures to netted sensors and computer networks. Finally, the focus on spontaneous development of patterns bridges the study of distinct components and the study of systems with many interacting com-

ponents. It thereby connects reductionism to complexity and emergence (3).

Is Anything Not Self-Assembly?

“Self-assembly” is not a formalized subject, and definitions of the term “self-assembly” seem to be limitlessly elastic. As a result, the term has been overused to the point of cliché. Processes ranging from the non-covalent association of organic molecules in solution to the growth of semiconductor quantum dots on solid substrates have been called self-assembly. Here, we limit the term to processes that involve pre-existing components (separate or distinct parts of a disordered structure), are reversible, and can be controlled by proper design of the components. “Self-assembly” is thus not synonymous with “formation.”

Types of Self-Assembly

There are two main kinds of self-assembly: static and dynamic. Static self-assembly (S) (Table 1; Fig. 1) involves systems that are at global or local equilibrium and do not dissi-

pate energy. For example, molecular crystals (4, 5) are formed by static self-assembly; so are most folded, globular proteins. In static self-assembly, formation of the ordered structure may require energy (for example in the form of stirring), but once it is formed, it is stable. Most research in self-assembly has focused on this static type

In dynamic self-assembly (D) (Table 1; Fig. 2), the interactions responsible for the formation of structures or patterns between components only occur if the system is dissipating energy. The patterns formed by competition between reaction and diffusion in oscillating chemical reactions (6, 7) are simple examples; biological cells are much more complex ones. The study of dynamic self-assembly is in its infancy.

We define two further variants of self-assembly. In templated self-assembly (T), interactions between the components and regular features in their environment determine the structures that form. Crystallization on surfaces that determine the morphology of the crystal is one example (8, 9); crystallization of colloids in three-dimensional optical fields is another (10). The characteristic of biological self-assembly (B) is the variety and complexity of the functions that it produces.

Common Features of Self-Assembly

Self-assembly reflects information coded (as shape, surface properties, charge, polarizabil-

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