Morphology of Complex Materials - Winter 2006

A Report on

HIERARCHICAL CONSTRUCTION OF MACROMOLECULES

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Abstract

A brief review of the study on hierarchical construction of macromolecules done by various authors is presented in this report.

Introduction

The breadth of structure and function displayed by the molecules of biology is remarkable, considering that there are only three major biopolymer backbones (proteins, ribonucleic acids, and polysaccharides); nature vividly teaches that copolymer sequence is a powerful way to meet diverse chemical challenges. It is reported that, most of the interesting functions carried out by bio-macromolecules, such as molecular recognition, information storage, and catalysis; involve stable, compact solution structures that approach conformational uniqueness. These high molecular weight macromolecules might be described as glassy-like, nanometer-sized particles that are suspended in solution and consist of one to, at most, a few chains. The spatial position of most of the backbone atoms is fixed, except for minor fluctuations about their equilibrium coordinates. There is also a congruency between particles having identical or even similar sequences. The surface of these particles includes three-dimensional, molecular-sized crevices lined with information-rich surfaces, and it is from here that affinity, specificity, and catalytic activity spring forth [1].

Many natural and man-made materials exhibit structure on more than one length scale; in some materials, the structural elements themselves have structure. This structural hierarchy can play a large part in determining the bulk material properties. Understanding the effects of hierarchal structure can guide the synthesis of new materials with physical properties that are tailored for specific applications [2].

When comparing natural and artificial macromolecular systems, it becomes apparent that although polymer chemistry is frequently considered a mature discipline, many features prominent in biological systems are absent in their synthetic counterparts. While polymer science has made tremendous progress over the last half century in controlling primary

structure by developing controlled/living polymerization processes, hierarchical structural organization of conformationally defined macromolecules using concepts from the emerging field of supramolecular chemistry has only recently begun [3].

Structural Hierarchy in Natural and Synthetic Macromolecules

In proteins – the principal machinery of life–structure, and thus function, is generated using a hierarchical construction plan [3]. A pictorial view of the four levels of structural hierarchy in proteins vis-à-vis synthetic polymers is presented in Figure 1.

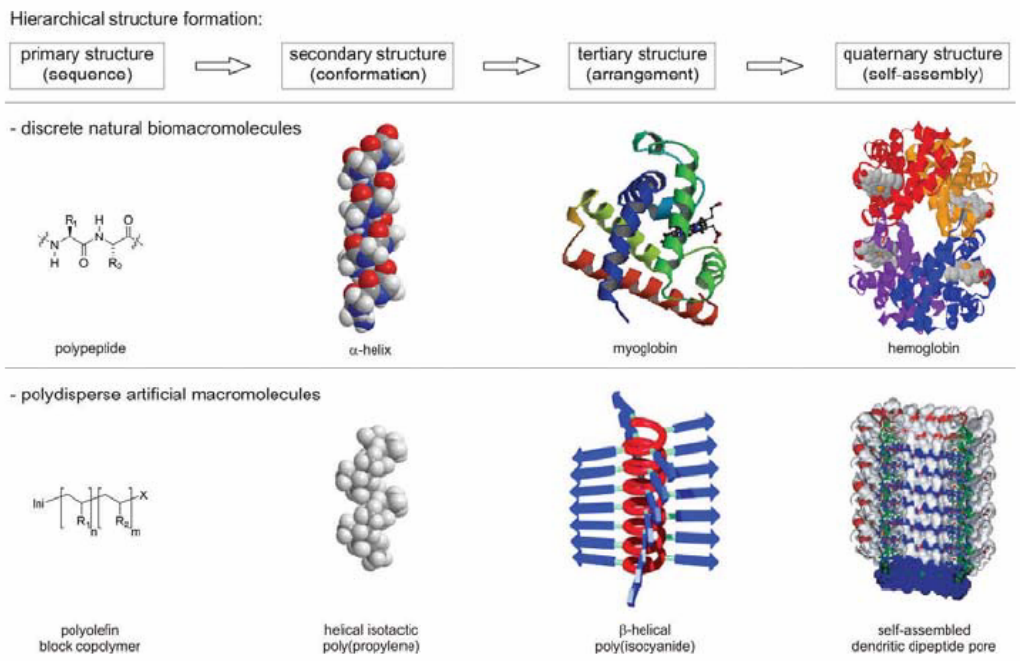

Figure 1 Hierarchical levels in natural and synthetic macromolecules [3].

(i) Primary Structure:

Peptide sequence or amino acid sequence is the order in which amino acid residues, connected by *peptide bonds*, lie in the chain. The sequence is generally reported from the N-terminal end containing free amino group to the C-terminal end containing free carboxyl group. Peptide sequence is often called protein sequence if it represents the primary structure of a protein [4].

At the primary structure level, different amino acid monomers are covalently connected to yield the desired peptide sequence. While monomer repeat-units are bonded covalently leading to long synthetic polymers. These generally are considered to be building blocks of higher level functional macromolecules.

(ii) Secondary Structure:

Secondary structure in biochemistry and structural biology describes the general three-dimensional form of local regions or overall shape of biopolymers. At this level, regions of primary strand are folded into well-defined chain conformations, using non-covalent interactions within the strand and with the environment.

The secondary structure of a protein may include regions of *α-helices*, *β-sheets*, *turns*, and *random coil*, or a few less common structures. Secondary structures can often be identified by circular dichroism spectroscopy. Nucleic acids also have secondary structure, most notably single-stranded RNA molecules [4].

(iii) Tertiary Structure:

The tertiary structure of a protein is its overall shape, involves the relative arrangement of secondary structure motifs within the same strand, for instance by introducing specific turns. The tertiary structure is held together primarily by hydrophobic interactions but hydrogen bonds, ionic interactions, and disulfide bonds are usually involved too.

All protein molecules are simple unbranched chains of amino acids, but it is by coiling into a specific three-dimensional shape that they are able to perform their biological function. The tertiary structure that a protein assumes to carry out its physiological role inside a cell is known as the native state or sometimes the native conformation.

A protein assumes tertiary structure by "folding". An important type of chemical bond involved in stabilizing the tertiary structure of many proteins is the *disulfide bond*.

Conventionally, tertiary structures are deduced through crystallography or multidimensional NMR [4].

(iv) Quaternary Structure:

Many proteins are actually assemblies of more than one protein (polypeptide) molecule, which in the context of the larger assemblage are known as protein subunits. In addition to the tertiary structure of the subunits, multiple-subunit proteins possess a quaternary structure, which is the arrangement into which the subunits assemble. Examples of proteins with quaternary structure include hemoglobin, DNA polymerase, and ion channels.

In addition to these levels of structure, proteins may shift between several similar structures in performing of their biological function. In the context of these functional rearrangements, these tertiary or quaternary structures are usually referred to as "*conformations*," and transitions between them are called conformational changes [4].

Within the last few years, a conscious effort has been made to design macromolecules with specific shapes (mostly spherical and cylindrical geometries), defined nanoscale dimensions, and tailored interior and exterior functionalities. Such macromolecular building blocks will play a key role in nanofabrication as top-down and bottom-up approaches merge.

Several design concepts have been developed to synthesize desired nano-objects, with most making use of directed and nondirected noncovalent interactions. For example, macromolecules with stable secondary structures in solution, or '*foldamers*', have received increasing attention on the one hand, while on the other, *'supramolecular polymers'* based on strong intermolecular interactions such as quadruple hydrogen bonding have been developed. It turns out that a combination of covalent and noncovalent synthesis is best suited to the preparation of shape-persistent objects of finite dimension in the nanosize range [3].

Foldamers [1]

Hill, D. J., et al., in their review article, a foldamer is defined as any oligomer that folds into a conformationally ordered state in solution, the structures of which are stabilized by a collection of noncovalent interactions between nonadjacent monomer units. There are two major classes of foldamers:

(i) *Singlestranded foldamers* that only fold (peptidomimetics and their abiotic analogues) and

(ii) *Multiple-stranded foldamers* that both associate and fold (nucleotidomimetics and their abiotic analogues).

Foldamers were related to an element of secondary structure, in the same way that tyligomer (Tyligomer is derived from *tyligos*, meaning "to fold", and *meros*, meaning "part" (i.e., a structure consisting of folded parts)) related to a tertiary or quaternary conformation.

Noncovalent interactions involve much weaker and reversible interactions than covalent linkages, which allows for the exploration of many chain conformations during the folding reaction. The net strength of the nonadjacent contacts that determine the thermodynamics of folding are essentially the differences between the strengths of the chain-chain and the solvent-chain interactions. It is reported that if solvent-chain contacts are stronger than chain-chain contacts, the molecule will not fold; as in the case of denaturing solvents. A subtle balance then exists in solvent-foldamer interactions; the solvent must solvate the molecule without competing for nonadjacent contacts while providing the chain with an environment in which to undergo the folding reaction.

The formation of unique, folded structures requires the presence of favorable nonadjacent chain-chain contacts or unfavorable chain-solvent forces. For oligomers containing residues that are poorly solvated, collapse to a set of compact conformations can occur before the folded state is populated. In a protein, the minimization of the solvophobic force between apolar residues and polar solvent, namely, water, lowers the free energy of the protein-solvent system and is the primary driving force for collapse. This collapse

minimizes the unfavorable solvation interactions and maximizes whatever favorable intrachain interactions exist, typically involving electrostatic and van der Waals forces. There is usually a gain in entropy for the solvent, since a higher degree of solvent ordering around the chain segment is required to solvate solvophobic segments than would be required to solvate solvophilic segments. The solvophobic collapse is then caused by a free energy gradient-having both entropic and enthalpic origins-toward states whose structures have a minimum of solvophobic segment-solvent contacts.

Thermodynamics of Folding:

Hill, D. J., et al. explained the thermodynamics of folding based on the Tetramer Toy Model (TTM), which is a 2-D square lattice chain consisting of two types of monomers, H and P (Figure 2). The TTM is a simplest model that captures many of the key features of the folding reaction. The model assumes a favorable interaction of magnitude ϵ between neighboring nonbonded H monomers. In this model there are four possible conformations exits, one of which has energy ϵ lower than the other three (Figure 2).

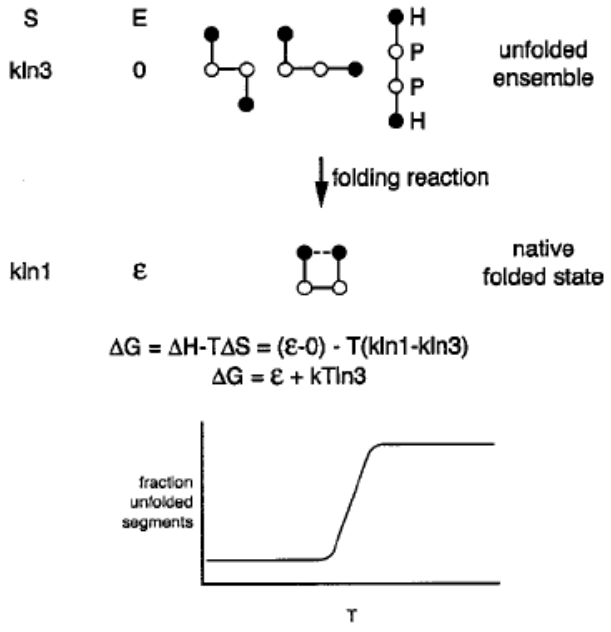

Figure 2. 2-D lattice Tetramer Toy Model. Black circles represent solvophobic repeat units (H) and open circles polar repeat units (P). The sigmoidal plot shows the fraction of folded molecules as a function of temperature.

The three unfolded conformations make up the unfolded ensemble, and the single collapsed structure is the folded state. It is found that there are fewer than ω^N (3^4) conformations for this system. This number is not reduced by excluded volume effects but by symmetry and the fact that only nonterminal monomer units have ω available conformations. Much of the thermodynamics of simple foldamers can be predicted by this model.

The size of the unfolded ensemble and the large number of potential folding pathways connecting this ensemble to the folded state suggest a statistical approach to the problem of folding. The thermodynamics of the folding reaction was explained using statistical mechanics, using partition function Z, which is given by eq 1 where $n(E)$ is the number of states that have an energy of E, and kT refers to the product of Boltzmann's constant and the temperature. The partition function is the Boltzmann-weighted sum of all the states, which for the TTM is given by the last term of eq 1.

$$Z = \sum_i e^{-E_i/kT} = \sum n(E) e^{-E/kT} = 3 + e^{-\epsilon/kT} \quad (1)$$

The fractions of the population in the unfolded and folded states at equilibrium for the TTM are given by eq 2, and the free energy of folding is given by eq 3 (the last term is specific to the TTM).

$$P(F) = \frac{e^{-\epsilon/kT}}{3 + e^{-\epsilon/kT}} \quad P(U) = \frac{3}{3 + e^{-\epsilon/kT}} \quad (2)$$

$$\Delta G_{\text{folding}} = -kT \ln K_{\text{eq}} = -kT \ln\left(\frac{P(F)}{P(U)}\right) = \epsilon + kT \ln 3 \quad (3)$$

The free energy of folding was derived by considering the ΔH and ΔS of the reaction. The enthalpy change is attributed to ϵ. The loss of entropy was calculated by taking the sum of the loss of entropy of each chain segment. As each segment has ω conformations available, the sum of the entropy lost over the whole N-long chain is approximately $-k \ln(\omega^N)$ or $-kN \ln \omega$.

At constant pressure and volume, the free energy change was given by eq 4.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \epsilon + kTN \ln \omega \qquad (4)$$

It was pointed out that this formulation had been used to experimentally estimate the entropy lost per chain segment and thus the average number of conformations available to each residue. From Eq 4, it was suggested the existence of folding temperature at which the population is evenly divided between unfolded and folded states or at which $\Delta G = 0$, called the folding (or melting) temperature (eq 5).

$$T_{\text{fold}} = \frac{-\epsilon}{kN \ln \omega} \qquad (5)$$

The free energy of folding becomes negative at a temperature where ω = 3 (kT ln 3), the entropy of the chain lost during folding, equals the enthalpic gain of folding, the energy gap between the folded state and all other states. A plot of the fraction of the population that is in the unfolded state as a function of temperature shown in Figure 2 has a sigmoidal curve that is indicative of the cooperative nature of this transition. Although the very term indicates the cooperation of two or more interactions, the transition of this small single-interaction system is cooperative in the sense that the system has a tendency to be either completely unfolded or completely folded. It was also reported that such transitions were observed for biopolymers, especially small, rapidly folding globular proteins.

The authors were of the view that the simple TTM model captures some of the essential features of the folding reaction and a key requirement of the folding system, namely, the large energy gap between the folded and unfolded states. This is clearly only a gross view of the folding reaction, which despite its complexity is just the process of going from a large number of relatively high-energy conformers to a very small number of low-energy conformers.

For these reasons, the authors explained the folding reaction in terms of free energy surface (FES), Some examples of representative FESs are given in Figure 3, including that for the lattice model (Figure 3a). This particular surface, consisting of a single, low-energy conformer distinct from the ensemble of nearly isoenergetic unfolded conformers referred to as the 'golf-course' landscape.

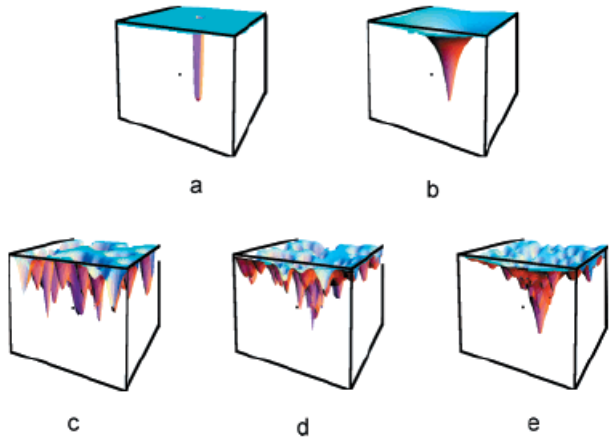

Figure 3. Free energy surfaces or "landscapes". (a) The "golf-course" energy landscape, (b) the smooth funnel, and (c-e) rugged surfaces where c has no energy gap and e has a large energy gap.

Each accessible conformation lies at the bottom of local vibrational and torsional energy wells, and their energies will also be dependent on nonadjacent interactions such as electrostatic and van der Waals forces between nonneighboring chain segments and side chains. These nonadjacent interactions can be both energetically favorable and unfavorable. The folded state of a well-designed foldamer minimizes the unfavorable interactions and maximizes the favorable ones. Because small changes in local structural parameters, such as rotation around a bond, can bring previously separated parts of the molecule together, thereby introducing many new contact energies, the FES can be very rugged. This is not usually the case for small homo-oligomeric systems because of the relatively small number (compared to a biopolymer) of random intrachain interactions that generate the ruggedness. These systems have FESs such as that in Figure 3b, a smooth funnel.

Longer chains, however, are capable of great ruggedness. Figure 3c depicts a completely rugged landscape with no single conformation dominating the thermal equilibrium mixture. Such rugged surfaces are typical of random heteropolymers, and an extremely poorly designed polypeptide would be expected to exhibit such an FES. Figure 3d shows a very rugged funnel, while Figure 3e depicts a classical rugged funnel typical of good folders having tertiary structure, such as globular proteins.

The authors conclude that those systems having FESs such as Figure 3d might be expected to fold but more slowly than those having funnels such as Figure 3e since the greater depth of nonnative wells slows eventual escape to the folded state.

Supramolecular Chemistry

Jeffrey S Moore [5] in his article reasoned that the polymer properties can be controlled through molecular engineering is one factor motivating vigorous research activity in the area of new molecular architectures called supermolecules (macromolecules whose monomeric units are held together by non-covalent forces). Because supramolecular chemistry involves reversible ordering and disordering processes, it is reasonable to expect that a high level of structural control can be attained for molecular materials constructed in this way.

The author described four processes that affect the ordered state of molecular materials: *covalent synthesis* (the process that determines molecular architecture), *self-assembly*, *self-organization*, and *induced organization*. Combinations of these different processes can provide a logical scheme to classify the states of order in molecular materials. Relevant architecture-defining parameters are molecular size and size distribution, topology (i.e. bonding connectivity) and stereochemistry, shape and shape persistence, chemical anisotropy (e.g. the Flory-Huggins interaction parameter, χ), and the spatial distribution of chemically distinct segments.

Traditional polymers are large covalent molecules, while supramolecular polymers often consist of small molecules held together by noncovalent interactions. Between these

extremes is the structurally diverse class of '*mesoscopic molecules*' (mass range ≈ l-10 kDa). Mesoscopic molecules not only encompass oligomers, but also include more topologically diverse architectures such as oligomeric macrocycles and dendrimers (cyclic and branched molecular topologies). One reason for interest in mesoscopic molecules is the ability to engineer their architectures into shape-persistent, size-specific objects that can overcome the entropic loss inherent in molecular ordering. In other words, their large and well defined molecular surfaces can define multiple interactions for highly cooperative self-assembly.

Self-assembly and self-organization are the spontaneous processes that impart order to molecular materials. Although both processes rely on supramolecular interactions, it is useful to distinguish these two terms. Molecular self-assembly is the thermodynamically controlled construction of supermolecules and involves designed, atom-specific noncovalent interactions. The resulting aggregates have a definable supramolecular constitution. Self-assembly may lead to finite structures (e.g. hydrogen-bonded dimers) or it may create extended supermolecules (e.g. 1D chains, 2D sheets, 3D networks).

Self-organization, on the other hand, is the spontaneous collective ordering of molecules or supermolecules into many-molecule ensembles, including equilibrium phases. Self-organization may be dominated by entropic factors (e.g. ordered fluid phases and microphase-separated block copolymers) or by repulsive or attractive noncovalent interactions. Regardless of these details, the interactions responsible for self-organization are less specific (i.e. less directional, less selective) than those responsible for self-assembly. Unlike self-assembly, there is no definable supramolecular bonding connectivity that one can associate with the self-organized structure.

The final means by which order arises in polymeric materials is through external factors. The term 'induced-organization' used by the author was to distinguish extrinsically derived order from that which arises through spontaneous processes. Induced-organization may, for example, come about by the mechanical forces encountered during polymer processing, and may also be the result of external fields (e.g. orientation of

polymers in an electric field) and of surface-induced organization. The author pointed out that many of the so-called 'self-assembled' systems referred to in the literature (e.g. self-assembled monolayers) are at least in part the result of surface-induced organizations.

Supramolecular Polymers

In recent time, there has been growing activity to develop supramolecular polymers. From molecular biology, the large molecules provide fertile ground for seeding sophisticated supramolecular design. For example, sequence-specific peptide chains store an enormous amount of information that can direct the complex assembly of multi-molecular components [6].

Moore [6] explained the *three aspects* of supramolecular chemistry need in discussing polymer molecules.

First, there is a topological aspect that deals with the self-assembly of chains and networks by reversible association of bifunctional or multifunctional monomers through specific non-covalent interactions e.g. hydrogen bonds.

Second, supramolecular polymers can be formed by multi-molecular self-organization of mesoscale molecules based on ''non-specific'' interactions. A biological example would be the aggregation of quasiequivalent protein molecules to form microtubulin 'polymers'.

The third aspect involves intramolecular supramolecular polymer chemistry and deals with the creation of order within a single molecule, i.e. the folding of chains into defined conformations. Internal order can bestow a macromolecule with precise size and shape as well as high-definition molecular surface features. These solvent exposed surfaces in turn can be used to guide higher order multi-molecular assembly.

The author envisaged that the most sophisticated supramolecular constructions would probably rely on combinations of these various aspects of supramolecular chemistry.

(i) Self-assembly of bifunctional monomers and telomers:

It is believed that the construction of chains and networks by reversible association of bifunctional or multi-functional monomers (either small molecules or telomers), involve specific non-covalent interactions. Recently Meijer et al. [7] reported their work based on this approach. The readily available 2-ureido-4-pyrimidone was found to strongly dimerize in a self-complementary quadruple hydrogen bonded array.

These units were used as the associating end groups in the preparation of linear supramolecular chains as shown in Figure 4, and supramolecular networks. The molar mass of these polymers was found to be very high compared to normal condensation polymers as a result of self-complementarity, the lack of side reactions during polymer formation, and the high dimerization constants. Polymer-like behavior was observed even in dilute solution.

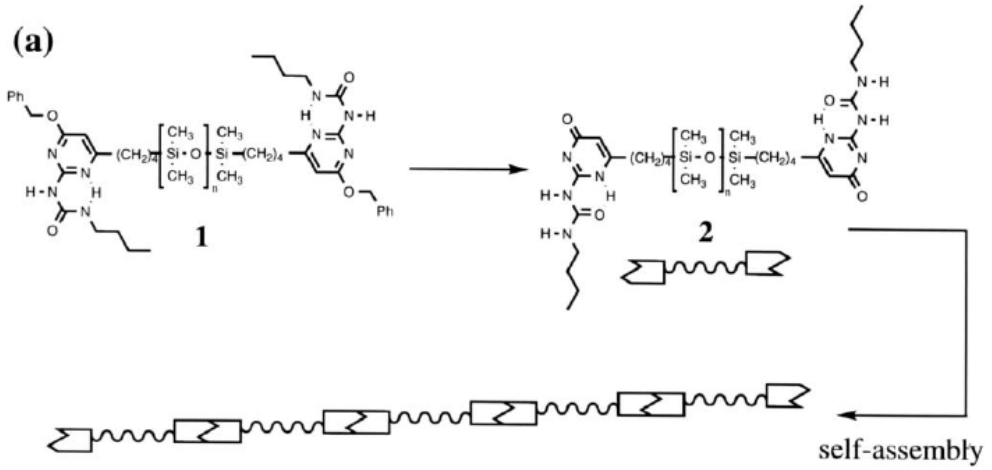

Figure 4 Self-assembly of supramolecular polymer chains. 1 Urido-pyrimidone bifunctionalized siloxane (Mn=6 kDa) gives telomer 2 upon debenzylation [7].

In another interesting work reported by Rebek and coworkers [8] described self-assembling polymer architectures referred to as polymeric capsules or ‘polycaps’ as shown in Figure 5. These structures formed by spontaneous association of bifunctional

monomers consisting of a pair of calix-4-arene tetraureas covalently connected through their lower rims 4-6 (in Figure 5).

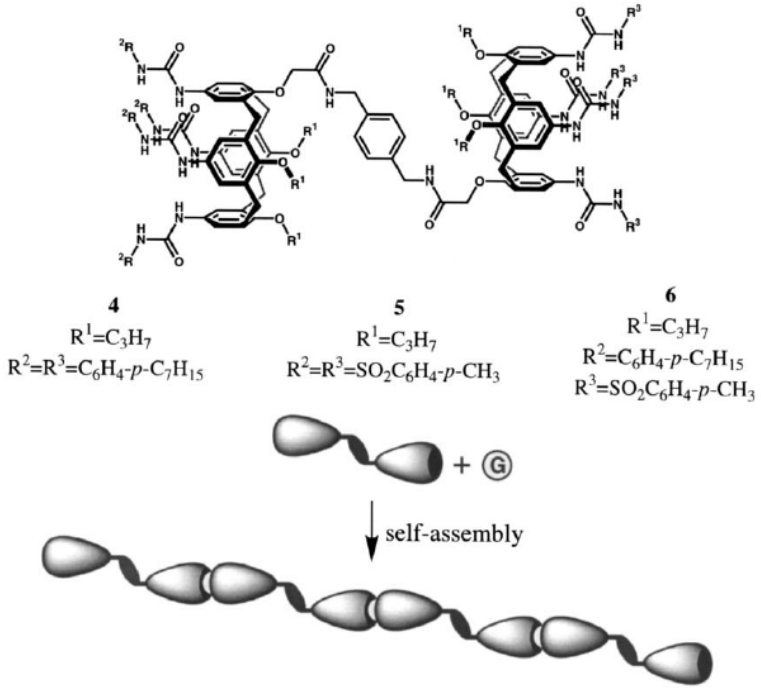

Figure 5 Bifunctional monomers 4 – 6 self-assemble into polycaps upon addition of an appropriate guest, G [8]

Encapsulation of small-molecule guests, G, triggered the formation of linear supramolecular polymers. Molecular recognition by encapsulation is largely determined by the volumes of the guest and host and binding is most favored when the ratio of guest volume to host volume is in the range of 0.55:8. Homodimeric capsules of aryl urea calix-4-arenes and homodimeric capsules of sulfonyl urea calix-4-arenes disproportionate to form the corresponding heterodimers; thus, polymer chains assembled from 4, 5 or from 6 (in Figure 5) alone acquire alternating monomer order along the supramolecular backbone. The authors also showed that this propensity to form heterodimers could be combined with multifunctional building blocks to spontaneously construct discrete nano-assemblies.

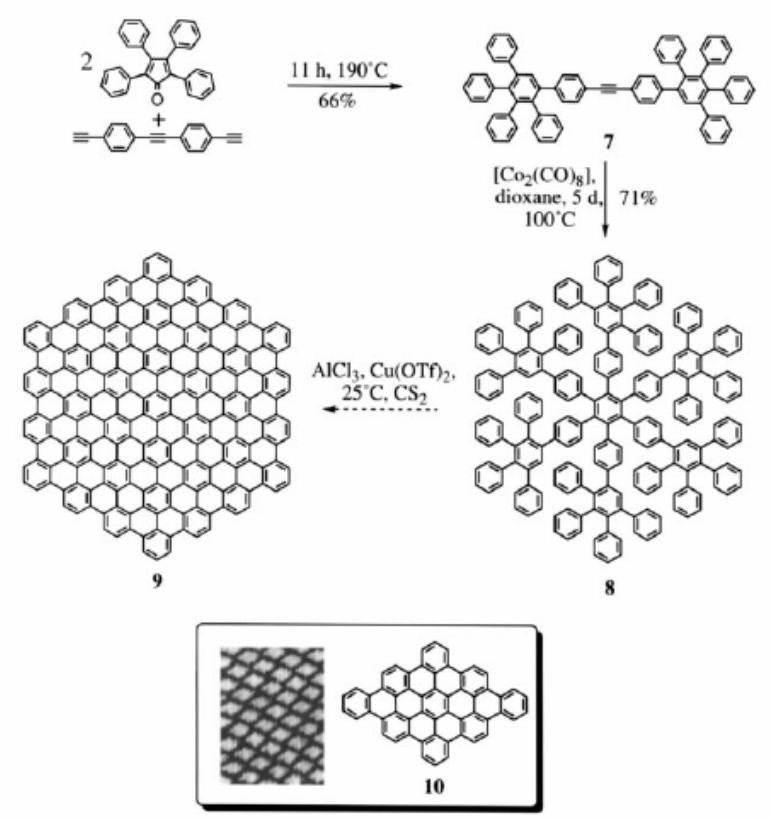

Figure 6 Intermolecular Diels-Alder cycloaddition, cobalt-mediated cyclotrimerization, and oxidative cyclodehydrogenation are used in tandem to synthesize giant polycyclic aromatic hydrocarbons. The boxed inset shows an STM image of a monolayer of 10 sublimed onto [001] MoS_2 in ultrahigh vacuum at 550-650°C [9].

(ii) Shape control and self-organization of mesomolecules:

In recent years, great attention has been paid to the design and study of mesoscale molecules possessing well-defined shapes and high-definition surfaces leading to self-organized structures. Müllen et al. [9], reported giant polycyclic aromatic hydrocarbons, as shown in Figure 6, constructed by combinations of *i)* Diels-Alder reactions involving alkynes and tetraphenylcyclopentadienone; *ii)* dicobaltcarbonyl-catalyzed cyclotrimerization; and *iii)* oxidative cyclodehydrogenation. The solubility of branched intermediates such as 8 (as shown in Figure 6) and even larger dendrimers 10 (as in Figure 6) is remarkably high.

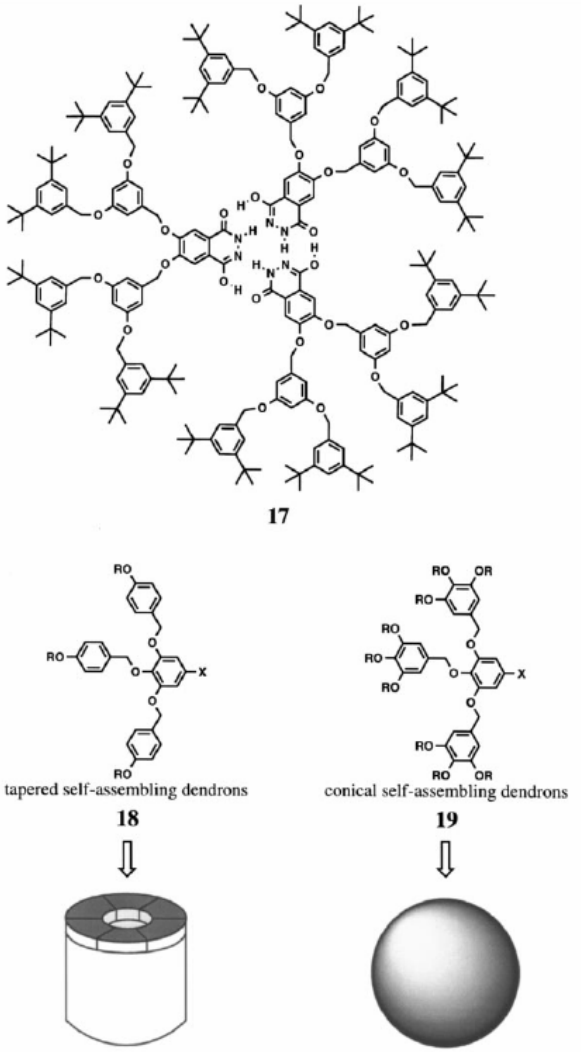

Figure 7 The production of finite supramolecular polymers using closed assemblies. Trimeric disc 17 is formed by self-assembly in solution [10]. Conically-shaped dendrons 19 self-assemble into spherical objects that self-organize on a cubic lattice [11].

The supramolecular organizations described above represent extended (i.e. infinite) phases and non-discrete supramolecular structures. An interesting trend that has recently emerged in the area of supramolecular polymer chemistry is the ability to construct finite-sized, discrete assemblies from mesoscale building blocks. Organizations of this sort are common in the biological domain but have been rare among synthetic macromolecules. This approach holds great potential for the production of nanostructured materials with integrated properties [10, 11]. At present, two strategies have emerged to achieve finite-sized discrete assemblies. The first shown in Figure 7, involves the creation of closed

structures such as cyclic aggregates (e.g. 17) or spherical supramolecular structures (e.g. 19).

The second strategy used in the design of discrete supramolecular objects is the frustration of infinite packings brought about by conjugating a pair of dichotomous segments. The existence of an optimized set of unfavorable and favorable contacts in the folded state has been called the "minimally frustrated" state.

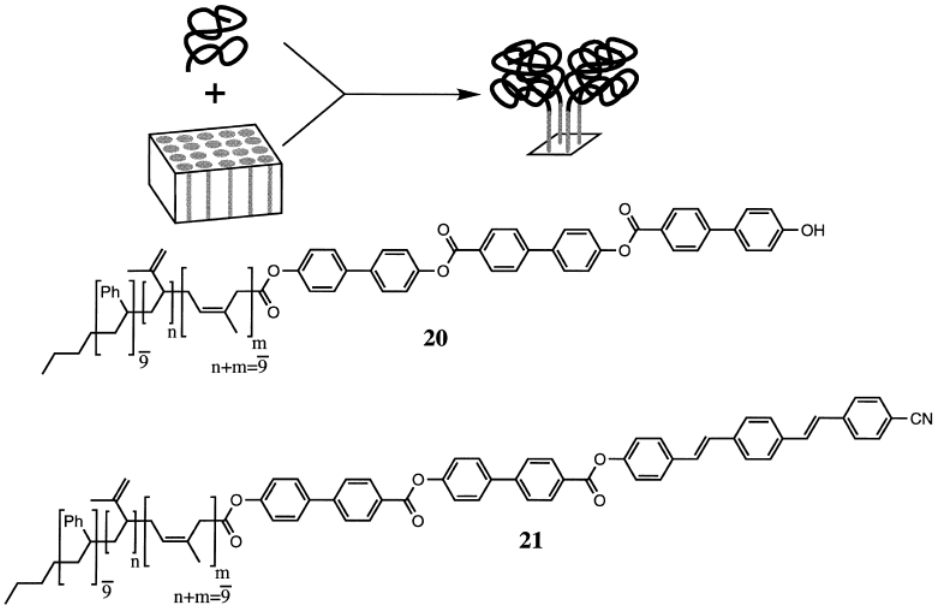

Figure 8 The schematic diagram illustrates the concept of producing finite supramolecular polymers by frustration of an infinitely periodic packing of rods. Rodcoil molecules 20 [12] and 21 [13] produce mushroom-shaped supramolecular polymers of nanoscale dimensions that are believed to result from this type of self-ordering mechanism.

The design concept is that one segment prefers to self-organize into an infinite phase while a second disordered segment blocks assembly through repulsive forces, as shown in Figure 8. Stupp and coworkers have shown that miniature triblock rodcoil polymers use this mechanism to produce discrete mushroom-shaped supramolecular nanostructures in the solid state. The rod-like segment prefers to crystallize into a layered structure but the volume and chemical mismatch of the covalently attached coil prevents extended periodicity from being acquired.

(iii) Folded macromolecules in solution:

It is believed that chain molecules provide the unique opportunity for an intramolecular variant of supramolecular chemistry folded macromolecules in solution. While ordered conformations in solution are commonplace among biopolymers, only recently have significant strides been made with synthetic chain molecules. Segments in a long linear chain are going to experience numerous intramolecular encounters in dilute solution. Individually these interactions may be weak although collectively they can become significant. Because the intramolecular interactions are coupled through constraints imposed by the backbone's covalent connectivity, the conformational transitions of chain molecules can exhibit high cooperativity. Cooperativity can provide a powerful principle for supramolecular organization and it is a design principle ideally suited to chain molecules [7].

Nelson JC et al. [14], shown that phenylene ethynylene oligomers (e.g. 22) as shown in Figure 9, can be driven to fold into helical conformations by solvophobic forces alone. On the basis of molecular modeling studies, the authors hypothesized that a key element in the design is *the molecular contact area per degree of conformational freedom*.

Maximizing this ratio should help insure stability of the folded structure as well as reduce degeneracy of the native state. According to this idea, the best monomer units would have a large, solvent-accessible surface area and be relatively rigid. Since van der Waals and solvophobic interactions are weak forces, they should be ideal for building up a folded structure that can undergo a cooperative conformational transition. Indeed, the stability of the folded conformation of 22 (as shown in Figure 9) was found to be dependent on chain length, solvent quality and temperature.

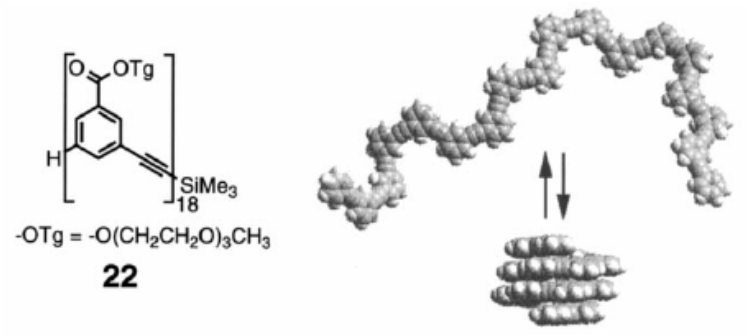

Figure 9 Oligo(phenylene ethynylene) 22 undergoes solvophobically driven folding into a helical conformation. The helix-coil equilibrium is illustrated with a space-filling model (side chains removed for clarity) [14].

Supramolecular Architectures

Franco Cacialli et al.[15] in their article reported the influence of molecular interactions is wide ranging, affecting properties as diverse as luminescence, electrical transport (charge hopping and, thus, interstrand mobility and spin coherence length), as well as chemical and mechanical stability. Accurate control of such interactions is needed to allow optimum exploitation of the properties of molecular materials, not only in today's most common optoelectronic devices such as lightemitting diodes (LEDs), field-effect transistors (FETs), and photovoltaic diodes (PVDs), but also in new or emerging applications, for example in the area of artificial noses and muscles or in general for nanoelectromechanical systems (NEMS). The authors were of the view that controlled and directed self-organization is the ultimate instrument for achieving such an aim, as it is only by mastering noncovalent interactions that control at the molecular level can be achieved.

Franco Cacialli et al., have developed Polyrotaxanes as insulated molecular wires and organic nanostructures. The use of polyrotaxane architectures offers a superior degree of control with respect to the design of the polymer substituents by threading luminescent, conjugated cores into nonconjugated insulating rings such as α or β-cyclodextrins (CDs). The resulting 'supra-molecules' are insulated molecular wires that displayed the basic semiconducting and optical properties of uninsulated chains and predicted that these can be used as molecular materials (for example in LEDs, as shown in Figure 10).

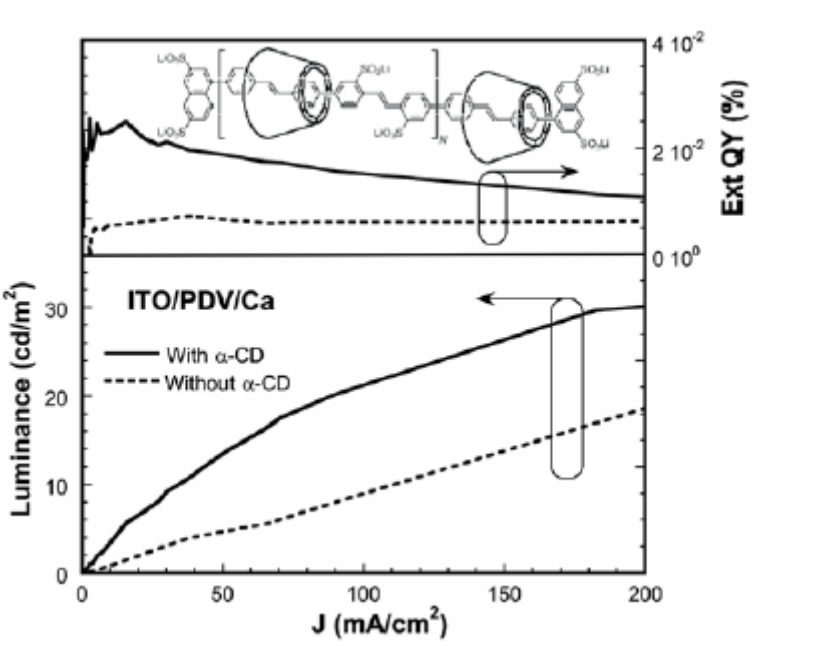

Figure 10 Electroluminescence of insulated (solid line) versus noninsulated (dashed line) molecular wires. External quantum efficiency (top panel) and luminance (lower panel) versus current density characteristics of poly(diphenylene vinylene) (PDV) and β-CD-PDV-based LEDs with ITO and Ca electrodes. The chemical structure of the insulated wires (i.e. threaded into the CD rings) is shown in the inset of the top panel. The insulated wires display higher efficiency and luminance up to high current densities [15].

Stefan Hecht and Anzar Khan recently have reported an approach to organic nanotubes that is based on intramolecular cross-linking of helically folded polymer backbones. Their concept (shown in Figure 11) is inspired by the hierarchical structural evolution in nature and involves polymerization of an appropriately functionalized monomer containing folding-promoting features as well as cross-linking units. The formed polymer strand (primary structure) is able to adopt a helical conformation (secondary structure), in which reactive groups are oriented within proximity to allow for subsequent covalent stabilization of the tubular nanoobject.

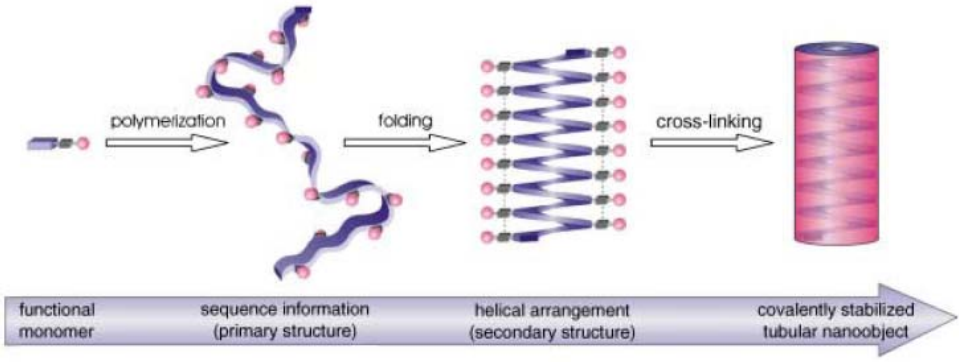

Figure 11. Formation of organic nanotubes by the intramolecular cross-linking of folded helical polymer backbones: Polymerization of a functional monomer carrying both solvophilic (magenta) and cross-linking groups (gray) generates a polymer strand that folds (solvophobically driven) into a helical conformation that is subsequently stabilized by covalent cross-linking using adjacent reactive groups [16].

Conclusions

Many materials exhibit hierarchical structure; the hierarchical aspects of structure are useful for descriptive purposes, for analysis and for synthesis [2]. Complex supramolecular organization demands information-rich molecules that display high-definition molecular surfaces. The mesoscale molecules illustrated above are recent examples from the synthetic world.

Folded polymers on the other hand, whose chemistry is determined by sequence, composition, chain-length, stereochemistry, and conformation, are the building blocks of biological assembly [7].

Mimicking nature's ability to produce complex arrangements should allow the use of information stored in single molecules to generate preprogrammed supramolecular arrangements. The route toward increasing complexity in such structures may be accomplished via exploitation of cooperative effects in systems regulated by weak interactions, thus paving the way for the fabrication of new supramolecular devices with unpredictable properties and unexpectedly high performance [15].

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