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Supramolecular Architecture

Synthetic Control in Thin Films and Solids

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Chapter 1

Supramolecular Architecture

Tailoring Structure and Function of Extended Assemblies

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This chapter will provide a brief overview about the various strategies aimed at structural control of extended assemblies. The systems under consideration evolve in their dimensionality from

- (i) Two-Dimensional Assemblies: Thin Films, to
- (ii) Layered and Low-Dimensional Structures, and
- (iii) Three-Dimensional Frameworks and Amorphous Networks.

Representative areas of research activity include selective monolayer assemblies on electrode surfaces, functionalized pillared layered materials, and assemblies of conductors, semiconductor clusters or nonlinear optical materials in three-dimensionally ordered hosts such as zeolites. Reference to articles in this book and to key contributions in the literature is given.

Dramatic advances in the areas of molecular synthetic chemistry such as organic chemistry or organometallics have led to a high level of control over molecular interactions. This becomes particularly clear in the field of molecular recognition where complexation, association and catalysis of organic and organometallic molecules can be fine-tuned almost as precisely as in biological systems, using creative combinations of ionic, hydrogen bonding, and other non-covalent interactions. The work of D. Cram and J.-M. Lehn represents a culmination of these efforts in the past decade. Representative systems include cavitands containing assemblies of aromatic rings,¹ and cryptands and spherands with multiple ligation sites for anions and cations.^{2,3} Organic molecular systems have probably been developed to the greatest extent; it is now possible to construct elaborate hierarchical molecules such as starburst dendrimers/arborols,⁴ and hyperbranched polymers,⁵ assemblies promoting non-covalent molecular association such as "molecular shuttles"⁶ or cyclophanes/aromatic complexes,⁷ and cyclodextrins⁸ that control access and orientation of reactants. Multiple hydrogen bonding for recognition and catalysis in organized systems is being used in Rebek's elegant di- and multiacid structures, and in nucleotide receptors.^{9,10,11}

The dreams of what could be possible very often have been inspired by Nature. This is particularly true for molecular interactions at various levels, for instance enzyme action for energy transfer and catalytic conversions, the senses, and, of course, the brain. However, the natural systems are characterized by enormous *complexity*, that is, by *hierarchies of structures and superstructures built up to functional units* such as

cell walls, muscles, nerves, etc. With all the impressive advances at the molecular level, we are only at the very beginning of a more extended control of chemical interactions in two and three dimensions. *Extended molecular interactions are highly important in catalysis, separations, control of energy flow, electrochemistry, optical effects, and ultimately the flow of information at the near-molecular level.* If we learn how to control the structure, properties and stability of desired supramolecular assemblies, many areas in materials science and technology such as microelectronics, optics, sensors and catalysis will benefit substantially. Representative areas of research activity include selective monolayer assemblies on electrode surfaces, functionalized pillared layered materials, and assemblies of conductors, semiconductor clusters or nonlinear optical materials in three-dimensionally ordered hosts such as zeolites.

The aim of this book is to bring together contributions from chemists who have embarked on research programs in this field which is highly challenging in both synthesis and characterization of the resulting structures. This chapter will provide a brief overview about the various strategies aimed at structural control of extended assemblies. Reference to articles in this book is given by indicating one author in parentheses. The systems under consideration evolve in their dimensionality from

- (i) Two-Dimensional Assemblies: Thin Films, to
- (ii) Layered and Low-Dimensional Structures, and
- (iii) Three-Dimensional Frameworks and Amorphous Networks.

Many of the structures contain "inorganic" as well as "organic" components; an indication that the desired systems often require a non-traditional approach for their synthesis. Although much of the work may be motivated by very different goals, the common challenge is the *synthetic control of chemical interactions at the "supramolecular" level.* Efforts are underway at different levels of dimensionality, from two-dimensional assemblies on surfaces, to layered materials, and finally complex three-dimensional structures, either crystalline or amorphous. In spite of the diversity, one central theme appears to dominate many strategies to assemble molecular units at higher levels. This theme is the "template" concept. Probably the most famous template of all is DNA itself which contains (almost) all information to duplicate the complex biological structures needed for successful life and reproduction. Templates are also useful and ubiquitous at less ambitious levels, for instance in making cookies, mass-producing cars, microchips, printing books, etc. Because it is very cumbersome to try to assemble significant numbers of moles atom by atom or molecule by molecule (even though recently the "molecule" "IBM" was assembled on a cold Ni(110) substrate by using a scanning tunneling microscope to move individual Xenon atoms into position),¹² some degree of automation in this ambitious endeavor is highly desirable. The template approach is extremely useful for this purpose, as will be demonstrated below and in the contributions throughout this book. The question then is how to motivate the species of interest to form the hierarchical structures desired.

Two-Dimensional Assemblies: Thin Films

Crystallization can be one of these techniques, however, to date it has been exceedingly difficult to predict and control the three-dimensional packing of larger molecules.¹³ In contrast, two-dimensional crystallization on surfaces such as organothiols on gold surfaces leaves one degree of freedom for design: the surface. Sulfur has a high affinity for gold and forces the alkane chains of the alkane thiol into a densely packed structure.¹⁴ The spatial requirements of the alkyl chain match well with the optimal packing arrangement of sulfur on the gold substrate. The polymethylene chains can be

terminated with many different functionalities to modify the wetting and/or reactivity of the newly formed surface (G. M. Whitesides). Thus, complex assemblies of functional groups in ordered organic films where redox centers are buried at different distances in the organic layer permit to control electron transport as a function of substrate size.¹⁵ These systems are promising model systems for modified electrodes, studies of friction, protein adhesion, and in the more distant future possibly microelectronic or optoelectronic devices.

At a slightly "thicker" scale, it could be shown that classical electronic functions such as diodes and transistors can be realized with thin layers of conducting polymers on microelectrode arrays.¹⁶ Attempts are now being made to reduce the dimensions of these arrays down to the molecular level. The proposed scheme for the design of a molecular diode is based on "orthogonal selfassembly",¹⁷ that is, preferential attachment of certain functional groups on different substrates (e.g., thiols on gold, isonitriles on platinum). If a microelectrode array with closely spaced alternating metal electrodes M_1 , M_2 , one of them reversibly blocked, is exposed to molecules L_1 -- L_2 , the molecules are expected to attach to one metal and bend over to the second after it has been unblocked.

Ordered thin films of layered metal phosphonates - inorganic analogs to Langmuir-Blodgett films - have been built using surface-attached phosphonates that were reacted with zirconium salts to replicate zirconium phosphate crystallization on a surface (T. E. Mallouk),¹⁸ and to afford multilayers with electron donating (e.g., tetrathienyldiphosphonic acid) and accepting interlayer functions (H. E. Katz). A related approach leads to mixed valence charge transfer compounds such as Ru(II)-pyrazine-Ru(III) assembled in multilayers (B. I. Swanson). Thin metal complex-containing layers can also be deposited using the Langmuir-Blodgett technique, for example with the system stearic acid/Ru(II)bipyridyl (M. K. De Armond). By modeling Nature's basic concepts for biomineralization, the group of P. C. Rieke has explored a variety of surface nucleation phenomena to grow thin crystalline layers of calcium carbonate, iron oxide, CdS and other materials on substrates such as modified polymers and functionalized, self-assembled monolayers. This approach mimics the functions of nucleation proteins and in some cases even permits to control the orientation of the crystallites deposited on the substrate.

Layered and Low-Dimensional Structures

If extended layered structures are considered, the template approach becomes even more obvious. Here the template is often an (inorganic) host, sometimes layered, that accommodates guest molecules in specific orientations, at certain distances, or stabilized against diffusion in cavities. Modified layered materials are therefore promising candidates for three-dimensional assemblies. The design of functionalized pillared metal compounds with, e. g., organic ion-exchange and ligating functions, is a main area of activity in A. Clearfield's group. In addition to clays, these compounds include group 4 and 14 phosphates, titanates, and antimonates. Enormous flexibility exists in the design of the pillaring groups, including diphosphonates with aromatic "rods" and sulfonate ion exchange capabilities, polyethers for ion conductivity, and polyimine chains as complexing agents within the galleries of the pillared material.¹⁹ Furthermore, the use of different precursors, such as simple phosphonic acid and one substituted with a ligating function offers the construction of mixed galleries which can enhance diffusion or reactivity in the layered material. The group of M. E. Thompson explores the intralayer reactivity of acyl chloride zirconium phosphonate with amines and alcohols to give layered amides and esters. Layered (clay) systems become porous and more stable under demanding conditions if intercalated with inorganic pillars such

as metal oxide clusters,²⁰ and they can incorporate porphyrin catalysts when synthesized from silicate gels containing water-soluble cationic metalloporphyrins (K. A. Carrado). If clays are intercalated with long-chain quaternary alkylammonium ions, attractive catalysts for three-phase reactions such as conversion of alkylbromides are formed. The surface of the layered material plays the role of a mediator at the liquid/liquid interface, bringing incompatible reactants into close proximity (T. J. Pinnavaia).

Inclusion polymerization of conducting polymers such as polyaniline or polypyrrole in layered structures such as FeOCl or V₂O₅ opens the way to new classes of hybrid systems (M. Kanatzidis). If the host lattice involves redox reactions such as in V₂O₅, mobile carriers are created on the host network which contribute to the overall conductivity of the system, to varying degrees such that n-type, p-type, and metallic behavior can be observed. Aniline could also be oxidatively intercalated into the layered proton conductor HFe(SO₄)₂ xH₂O (D. J. Jones).

"Soft chemistry" strategies are important for the design of metastable low-dimensional and open framework solids, for example by using redox processes (e.g., deintercalation of Li(I) from LiVS₂ to obtain VS₂)²¹ or acido-basic reactions, in order to avoid thermodynamic control typical for high temperature processes (J. Rouxel). A classical example is the synthesis of a new form of TiO₂ from the low-dimensional K₂Ti₄O₉ with K⁺ ions between titanium oxide ribbons.²² Acid ion exchange and heating replaces K⁺ with hydroxyl groups that are eliminated at higher temperature such that the Ti blocks are sealed to a new titanium dioxide. In another example, layered FeOCl can be used as a precursor to lamellar iron phosphonates by anchoring organophosphonates onto the FeO layers (P. Palvadeau). Electrocrystallization is another approach to low-dimensional molecular solids, where one of the ions is produced by redox reactions at the electrode to crystallize with a counterion present in solution (M. D. Ward). One finds that nucleation, morphology and stoichiometry can be controlled through manipulation of the electrochemical growth conditions.

Superlattices, consisting of several lattices stacked in a regular fashion with long-range order in the z-axis, are of great interest for their unusual quantum electronic and optical effects.²³ The design of these systems has typically required vacuum deposition methods, but extended artificial superlattices are now accessible through controlled electrocrystallization (J. Switzer). Alternating layers of different Tl-Pb oxides as thin as 3 nm could be deposited by changing the electrochemical (galvanostatic) deposition conditions in the same solution. The near-perfect match of the lattice parameters of these systems with varied Pb/Tl ratio is the basis for the successful epitaxial growth - another type of structural templating.

Multilayered repeating structures with potential applications in nonlinear optics have been grown on glass surfaces using a sequence of silane coupling agent, chromophore, and structural reinforcement with siloxane/polyvinylalcohol layers.²⁴ The scanning tunneling microscope allows unprecedented resolution in imaging and direct-writing of nanostructures (B. Parkinson). Surface modification techniques using the STM tip include large voltage pulses to field emit atoms from the tip or disrupt the substrate, deposition of matter from solution or gas phase, and the use of van der Waals forces to move atoms and pattern layered materials. This is exemplified in the interesting "etching" behavior of layered MoS₂ and SnSe₂ where single molecular layers can be sequentially removed in areas as small as 20 nm.

Three-Dimensional Frameworks and Amorphous Networks

Based upon their well-defined, crystalline pore architecture with channel sizes at molecular dimensions, zeolites are becoming increasingly attractive as hosts for a

variety of species and purposes. This increasing activity is also critically dependent upon recent advances in analytical techniques such as synchrotron X-ray powder diffraction, neutron diffraction, EXAFS, and solid state NMR. Researchers have now also begun to explore the fundamental kinetic aspects of intrazeolite model reactions such as CO and PMe₃ substitution at Mo(CO)₆ (G. A. Ozin) that was found to be first order. Resulting reaction parameters such as the entropy of activation permit conclusions about the nature of the transition state stabilized in the unique zeolite cavity. Intrazeolite diffusion and assembly of reactants is also key to understanding of electron transfer processes between photoexcited electron donors Ru(bpy)₃²⁺ and viologen acceptors (T. E. Mallouk). These systems can be described as *molecular diodes* and *photodiodes*. The quenching behavior indicates that electron transfer involves diffusion of the acceptor. More elaborate assemblies show that charge recombination can be slowed considerably by using the structural templating function of the zeolite host.

The interplay between acentric (zeolite) hosts and molecules with large hyperpolarizabilities as well as the stabilization of nanometer size II-VI, III-V semiconductor clusters in zeolites promise to become important strategies for assemblies with non-linear optical properties (G. D. Stucky). The sodalite structure, consisting of a three-dimensional periodic arrangement of truncated octahedra, is a highly crystalline host with great compositional variation for the packaging approach. Clusters encapsulated in these cages include Cd₄S, Zn₄S, Na₄³⁺, and Zn₃GaAs. Molecule-sized silver-halo clusters stabilized in different zeolites, in particular in sodalites,²⁵ show promise for optical data storage and sensor applications, while intrazeolite molybdenum oxide clusters²⁶ derived from Mo(CO)₆ are further examples of quantum-size materials stabilized by the zeolite host (G. A. Ozin). In these cases the hosts determine cluster structures and optical properties which are dramatically different from the corresponding bulk properties and even from those of colloidal semiconductors.

The molecule-sized zeolite channels are ideal hosts for stabilizing oligomers of thiophene²⁷ and single chains of conducting polymers such as polyaniline, polythiophene, polypyrrole and pyrolyzed polyacrylonitrile that are promising candidates for molecular electronic assemblies (T. Bein). The materials when recovered from the zeolite hosts are in a conducting state, while microwave absorption measurements indicate that in the absence of electrostatic host-guest interactions even the encapsulated species have significant carrier mobility.

Three-dimensionally ordered frameworks with structures sometimes derived from simple prototypes (e.g., PtS, diamond, rutile) have been constructed using an imaginative combination of metal coordination chemistry with certain geometries and rod-like or plate-like building blocks (Robson). This versatile approach leads to a large variety of fascinating structures with channels, cavities, and interpenetrating networks. For example, Cd(CN)₂ · 1.5 H₂O) · t-BuOH forms hexagonal channels (filled with the solvents) consisting of interconnected square-planar and tetrahedral centers at ratio 1:2. Some of the new frameworks contain porphyrin stacks, for example in (tetrapyrrolylporphyrinato)palladium · 2Cd(NO₃)₂ · hydrate, and variations of this theme may afford interesting catalytic applications.

Another type of three-dimensional assembly using not coordination but hydrogen bonding forces is more related to the molecular recognition studies in solution mentioned above (G. M. Whitesides). The reaction of melamine with isocyanuric acid forms a stable, 1:1 complex that features a two-dimensional honeycomb structure where each hexagonal unit of the lattice consists of a ring of three alternating cyanurate and melamine rings. This structure shows surprising temperature stability (450 °C) and is just one of many related, tape-like arrangements that form from similar complementary molecules via hydrogen bonding.

New approaches to the synthesis of known materials are in high demand for several reasons. Traditional solid state synthesis requires high temperature and

frequent grinding to allow sufficient interdiffusion of the reactants, thus the products are usually those with highest thermodynamic stability. In contrast, the deposition of alternating atomically thin layers of reactants allows interdiffusion at much lower temperature, and the nucleation of the resulting amorphous phase becomes the rate-limiting step such that metastable phases can be formed when their nucleation rate is faster than that of thermodynamically stable phases (D. C. Johnson). If the heat for the solid state reaction is chemically stored in the precursors, reaction times can be radically shortened from days to seconds (R. B. Kaner). Thus, layered molybdenum disulfide can be made in a metathesis reaction between MoCl_5 and Na_2S , where the reaction is driven by the stability of resulting sodium chloride. Related reactions can be devised for many other compounds such as metal and main group chalcogenides, carbides, oxides, silicides, and solid solutions.

Structural control can also be achieved in porous amorphous inorganic materials such as silicate glasses derived from alkoxy silanes. The structural parameters include pore size hierarchies described by fractal dimension, and pore volumes. Recent advances in sol-gel processing have made it possible to control porosity over wide ranges of narrow pore size distributions by varying the size and mass fractal dimension of the precursor polymer, aging conditions, the relative rates of drying and condensation, and the associated capillary pressure exerted on the gel network during drying.²⁸ The porous glasses are versatile hosts for a variety of organic dyes and reagents that allow the design of chemical sensors, enzyme-based catalysts, and optical devices (D. Avnir; Y. Haruvy). The latter groups have developed a trapping approach that holds the guest molecules in the gel-glass yet maintains access to a significant fraction of the guest molecules from solution.

In summary, fascinating new avenues towards the control of chemical interactions and physical properties in two- and three-dimensional systems are presently being explored. It is hoped that this book serves to disseminate recent research results and to stimulate new and extended activities in this young field of chemistry.

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