

Supramolecular chemistry: Functional structures on the mesoscale

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Supramolecular chemistry deals with the chemistry and collective behavior of organized ensembles of molecules. In this so-called mesoscale regime, molecular building blocks are organized into longer-range order and higher-order functional structures via comparatively weak forces. As one of the modern frontiers in chemistry, supramolecular chemistry heralds many promises that range from biocompatible materials and biomimetic catalysts to sensors and nanoscale fabrication of electronic devices.

For over 100 years, chemistry has focused primarily on understanding the behavior of molecules and their construction from constituent atoms. Our current level of understanding of molecules and chemical construction techniques has given us the confidence to tackle the construction of virtually any molecule, be it biological or designed, organic or inorganic, monomeric or macromolecular in origin. During the last few decades, chemists have extended their investigations beyond atomic and molecular chemistry into the realm of supramolecular chemistry. Terms such as molecular self-assembly, hierarchical order, and nanoscience are often associated with this area of research.

Broadly speaking, supramolecular chemistry is the study of interactions between, rather than within, molecules—in other words, chemistry using molecules rather than atoms as building blocks. Whereas traditional chemistry deals with the construction of individual molecules (1–100 Å length scale) from atoms, supramolecular chemistry deals with the construction of organized molecular “arrays” with much larger length scales (1–100 nm). In molecular chemistry, strong association forces such as covalent and ionic bonds are used to assemble atoms into discrete molecules and hold them together. In contrast, the forces used to organize and hold together supramolecular assemblies are weaker noncovalent interactions, such as hydrogen bonding, polar attractions, van der Waals forces, and hydrophilic–hydrophobic interactions.

First and foremost among the motivations for exploring supramolecular chemistry is the desire to synthesize new robust, functional, and technologically important materials by mimicking nature. In nature, organization on the nanometer scale is crucial for the remarkable properties and functional capabilities of biological systems. In biological ensembles such as collagen and enzymes, the combination of the individual molecular components is not solely responsible for their unique properties. Rather, their unique properties also depend heavily on the specific ordered spatial structures resulting from their molecular organization. Although biological materials can be harvested and modified, their fragility, limited availability, and highly evolved structures limit their utility. Instead, many chemists are seeking to imitate nature's supramolecular design motifs to generate large quantities of robust nanostructured materials in a facile manner. The potential applications for these materials range from new catalysts to biocompatible structures for tissue and bone replacement therapy.

A second impetus is the desire to design, using functional small-molecule building blocks, new synthetic materials that feature even more useful ensemble properties emanating directly from

nanoscale and microscale ordering. During the last decade, this idea has been successfully demonstrated by a number of researchers.

Lastly, the need for improved miniaturization and device performance in the microelectronics industry has inspired many investigations into supramolecular chemistry. It is conceivable that “bottom up” materials fabrication approaches based on supramolecular chemistry will provide a solution to the anticipated size limitations of “top down” approaches, such as photolithography, thereby providing the means to fabricate ultra-small electronic components. Perhaps more likely is that hybrid devices will become increasingly ubiquitous and important. These devices integrate the outstanding electronic and photonic properties of nonmolecular hard materials such as silicon to the excellent bio-recognition, chemical sensing, and related properties of designed, soft molecular materials to yield structures capable of performing disease diagnosis, environmental monitoring, controlled drug delivery, and so on.

Synthetic approaches to supramolecular chemistry can be categorized based on the nature of the molecular building blocks, i.e., whether they are organic or inorganic in nature, or whether they are small molecules or macromolecules. Small-molecule organic building blocks include molecular liquid crystals, hydrogen bonding molecules, catenanes, and rotaxanes (1, 2). These have been used to create supramolecular ensembles ranging from nanostructured catalytic reactors to electrochemically switched molecular shuttles. Macromolecular organic building blocks include phase-separated block copolymers and more recently dendrimers. These have been used to generate sophisticated ordered composites and to allow nanopatterning on surfaces. “Self-assembling” coordination compounds featuring ligand-functionalized porphyrins and related components have been a mainstay of inorganic supramolecular chemistry (3). More recently, semiconductor or metal nanoparticles have been used as “macromolecular” inorganic components for supramolecular arrays with interesting electronic properties.

Gin and coworkers (4, 5) reported their findings on the rational design and synthesis of self-organizing building blocks for the construction of nanostructured polymers and other organic materials. These building blocks include polymerizable thermotropic and lyotropic (i.e., amphiphilic) liquid crystals incorporating functional properties. Gin's group has exploited the unique self-assembly properties of polymerizable organic liquid crystals to construct nanostructured organic networks

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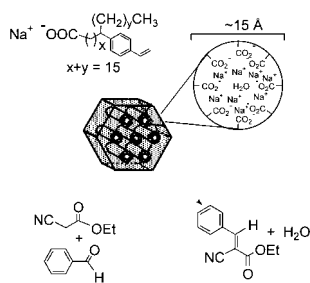


Fig. 1. A nanostructured heterogeneous base catalyst for the Knoevenagel condensation based on liquid crystals.

capable of heterogeneous catalysis, as well as nanoscale filtration. Other materials such as nanostructured composites, non-centrosymmetric polymers, and polymer-based sensors have been realized via this approach (Fig. 1).

Hupp, Nguyen, and coworkers at Northwestern University (6–8) have designed high-yield synthetic routes to a family of neutral, luminescent molecular boxes, in both square and rectangular motifs, via coordination of Re(I) corners by difunctional organic ligand edges (e.g., Fig. 2). Depending on the size of the edges, such structures can be constructed with cavities that range from $7 \text{ \AA} \times 7 \text{ \AA}$ to $20 \text{ \AA} \times 20 \text{ \AA}$ and $6 \text{ \AA} \times 25 \text{ \AA}$. In the solid state, these compounds feature exceptionally large void volumes because of the large cavity sizes and the absence of charge-compensating ions. As such, the molecular solids typically display good mesoporosity and an ability to function as high-capacity hosts for suitably sized guest molecules. Mesoporous solids can complex a variety of molecules and hence can be used as sensors for organic vapors. The interiors of comprising the materials also can be readily modified with a variety of chemical receptors to make the cavities more selective in molecular uptake. The molecular-box materials have been configured as thin-film chemo-sensory arrays by using capillary-driven microcontact printing. Sensing can be accomplished by monitoring guest molecule-induced changes in film luminescence, mass, or diffraction efficiency.

The Northwestern workers also have used the molecular boxes and related assemblies to encapsulate manganese-based olefin epoxidation catalysts (Fig. 2). The ability to tailor the resulting reaction cavities via framework binding of any of scores of chemically, sterically, and/or chirally demanding secondary ligands has enabled them to access a second-generation catalyst

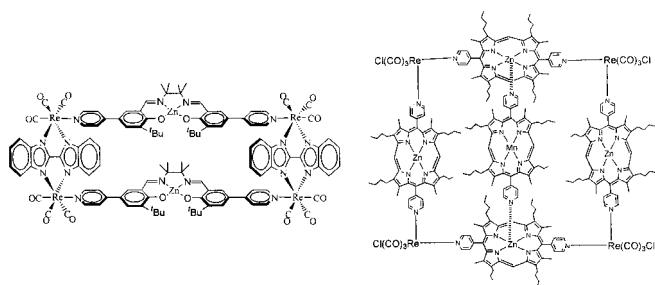


Fig. 2. Molecular boxes with variable dimensions. (Right) Featured is an encapsulated olefin-epoxidation catalyst.

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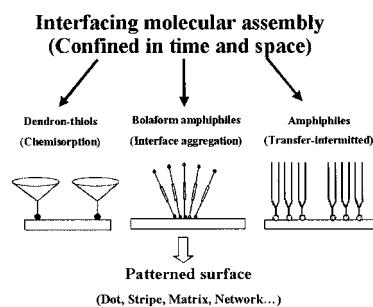


Fig. 3. Fabrication of patterned soft materials structures via interfacial self-assembly.

design menu of exceptional breadth. This “artificial enzyme” approach allows, or potentially allows, for substrate: (i) size-selective catalysis, (ii) shape-selective catalysis, and (iii) enantioselective catalysis, while also providing enormously enhanced catalyst stability (9).

Zhang’s group (10) used interfacial molecular assembly as the method of choice for fabricating various thin film-based devices and sensors using nanoscale patterns in the size range of 1 to 10^2 nm with controlled composition and molecular orientation. Chi and coworkers (11) used Langmuir–Blodgett techniques to transfer the amphiphile L- α -dipalmitoyl phosphatidylcholine to mica to form a patterned structure consisting of hydrophilic grooves 200 nm in width and hydrophobic stripes 800 nm in width. These patterned structures can then be used as matrices to incorporate many types of interesting materials, resulting in functional patterned materials (Fig. 3).

Going down in scale, Zhang’s group (12) has taken advantage of the interfacial aggregation properties of a bolaform amphiphile-bearing azobenzene compound to form ordered stripes on mica sheets. The ordered stripes are separated from each other by about 10 nm. In addition, the patterned surface structure can be systematically altered via exposure to UV irradiation (which induces a cis/trans isomerization of the azobenzene moiety).

To form patterned structures on the nanometer scale, Zhang and coworkers (13) chemisorbed thiol-containing polyether dendrons onto gold-covered slides to form patterned surfaces with nanometer-sized features and long-range order. They found that the patterned stripes are closely related to the size of the dendrons. The widths of the stripes derived from dendrons of generations 1–3 are about 2.3, 3.1, and 4 nm respectively. Using thiol-containing dendrons that feature both hydrophobic and hydrophilic periphery, they obtain honeycomb structures with pore diameters of ≈ 5 nm. They proposed that a confined nanoscale-phase-separation effect is responsible for the molecular organization at the interface.

In summary, principles of supramolecular chemistry can be applied to the facile synthesis of new mesostructured assemblies featuring long-range order and displaying useful functional behavior (molecular recognition and sensing, biomimetic catalysis, size and shape selective molecular transport, etc.). Further work on supramolecular materials fabrication will yield many additional examples of functional, self-organized assemblies, including assemblies displaying useful photonic and electronic properties.

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