NIRT Highlight (Theory, Modeling and Simulation)

Design of Nanoporous Molecular Square Catalysts using Multiscale Modeling

Nanoscale Chemical Factories

We have recently developed supported membranes that act as nanoscale filters, allowing small molecules to pass through, but blocking large molecules [1,2]. The membranes are built from "molecular square" subunits, each having identically sized 2 nanometer openings. The filters may have applications in chemical separations and in selective sensing of heavy metals, volatile organic compounds [3], and bio-markers (small proteins, etc.) relevant to human health. We have also recently reported that molecular squares can be used to encapsulate chemical catalysts to form assemblies that behave in solution as artificial enzymes, rapidly converting cheap chemical feedstocks into valuable precursors for pharmaceutical molecules [4]. We have now successfully combined the two ideas: Catalyst-containing squares have been organized as thin-film arrays of nanoscale reactors or factories, as shown conceptually in the figure below. Molecules passing through the factories are not only sorted on the basis of their size, but once sorted are processed chemically to convert them into building blocks for pharmaceuticals, high-performance polymers, and other useful material [5].

Why is it useful to assemble the nanoscale factories as extended arrays? First, the catalysts are tremendously stabilized by encapsulation within arrays. Rather than processing only 50 or 60 feedstock molecules before degrading, each array-encapsulated catalyst can process around a million molecules. Second, by behaving as nanoscale filters, the molecular-square arrays deliver to the catalysts only those feedstock molecules having the right pre-determined size; those that are larger than desired are completely excluded from the tiny factories. This means that the desired chemical product can be manufactured selectively, even if high-purity feedstocks aren't available. Third, unlike individual catalysts used in solution, the solid arrays can be separated from the reaction products simply by lifting the array out of the reaction solution.

Development of Molecular Modeling Tools

If the nanoscale factories can be further improved (higher throughput, selective manufacturing of right-handed versus left-handed mirror image molecules, even longer catalyst lifetimes) and if they can be adapted to a wide variety of chemical manufacturing processes, they will lower the costs of a wide range of specialized chemical manufacturing processes while also greatly decreasing any environmental impact of the processes. This development will require a better understanding of their properties on the microscopic level. Molecular modeling can be of great use for this purpose. Our recent modeling focus has been on development of a systematic approach to molecular modeling of molecular squares (that can be extended to other systems), as well as applying this approach to these systems.

Using force field simulations, we have preformed preliminary grand canonical Monte Carlo simulations to predict adsorption isotherms for various small molecules within crystalline arrays of small pyrazine and bipyridine squares. Molecular dynamics simulations have also

yielded a first look at diffusion rates in these systems. In addition, we have incorporated the porphyrin-specific implementation of the DREIDING force field into our multipurpose molecular simulation code, Music [6] and performed preliminary tests of the applicability of this force field to the porphyrin walls of related molecular "rectangles" of known experimental crystal structure. Currently, we are applying this approach to analyze possible conformations of the more interesting porphyrin molecular squares, for which crystallographic data are not available. We can then also study particular effects of various solvents on observed conformations and extend the analysis to molecular square behavior within supramolecular arrays to help optimize the experimental work.

For electronic structure calculations, our version of the Divide & Conquer linear-scaling density functional methodology has advanced on two fronts. First, atomic force algorithms are now used to determine equilibrium atomic geometries of molecular clusters to good precision. Extensions to the embedded cluster framework are underway. Second, the original DAC 1 distributed computing scheme was based upon a one-master/many-slave work model, which has the advantage of simplicity but is not optimum from the point of view of data base building and mining and from error recovery. We are now in an advanced stage of coding DAC 2, which is based upon a "worker-ant" model in which independent computational units seek tasks for which they are qualified. DAC 2 is also designed to exploit symmetry properties of periodic systems. We have completed initial surveys of electronic structure of molecular components of the simplest pyrazine and 4,4'-bipyridine molecular square frameworks, in conjunction with the force field modeling. From these we have extracted self-consistent atomic configurations and charges, for use in updating the molecular mechanics force fields, and have produced maps of electron density to guide more refined interpretations of bonding interactions. Preliminary studies have been completed on the Zn-porphyrin wall-structure components. Embedded cluster studies on the complete framework will next be undertaken, as will initial studies on molecular chemisorption, guided by the force field results.

References

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Arrays of Nanoscale Chemical Factories