Functional Nanostructured Molecular Materials

by Joseph T. Hupp and SonBinh T. Nguyen

There has been tremendous recent interest in the design and assembly of porous nanostructured materials.[1] Synthetic approaches range from coordination-polymer formation to surfactant-templated alumino-silicate growth to semiconductor nanoparticle aggregation, while functions include chemical catalysis, chemical sensing, energy storage, and energy conversion. A promising but thus far largely neglected synthetic approach is the assembly of porous materials from discrete molecular building blocks—especially building blocks consisting of cyclic, nanoscale cavity-containing coordination compounds.

The molecular approach is especially useful for circumventing two common difficulties with many of the conventional approaches. The first is the collapse of channels upon removal of solvent from the porous solid. While the units comprising molecular solids are held in place only by weak forces (mainly dispersion interactions), molecules defining individual cavities are beneficiaries of substantially stronger interactions (covalent and coordinate-covalent bonds). Indeed, the interactions are strong enough to preclude cavity and channel collapse. The second complication is interpenetration such that vacancies—for example in a lattice polymer structure—are occupied by a geometrically orthogonal, but structurally identical structure (or in some cases, by multiple intersecting and interpenetrating structures). The lattice interpenetration phenomenon is generally thermodynamically driven, reflecting the free-energy gains achievable by maximizing van der Waals interactions. While an equivalent molecular phenomenon, cycle catenation, is occasionally encountered, the isolated assembly of molecular building blocks via intentionally substitution-inert coordination chemistry, precludes catenation and leads to open, high porosity, high void volume solids.

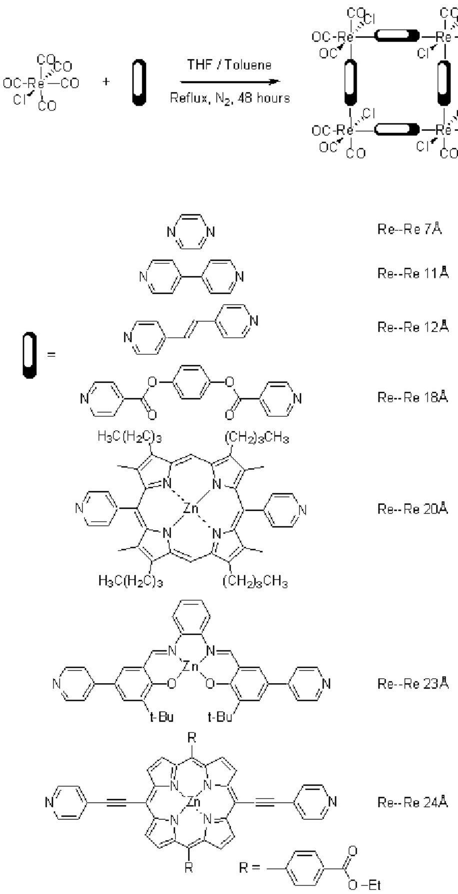


FIG. 1. Directed assembly of building blocks for molecular materials.

The starting point for materials synthesis of this kind is the construction of appropriate cavity-containing coordination compounds (*i.e.*, discrete molecules). Over the past dozen years an enormous number of molecules of this kind have been synthesized, albeit, nearly always with isolated-molecule, solution-phase applications in mind.[2,3] Many of the reported syntheses rely upon preprogramming of synthons, leading to a directed-assembly approach that often yields the desired molecules in a single step. Figure 1 illustrates a variant used extensively in our laboratory.[4] In the scheme, rigid or semi-rigid bifunctional edges coordinate exclusively in a cis geometry to an octahedral metal site. The preference for cis coordination is a direct consequence of a classic carbonyl trans-labilizing effect in the pentacarbonylchloro rhenium starting material. The cis geometry configures the component ligand "edges" at roughly 90° to each other, predisposing the components to cyclize as squares. Using this approach, square frameworks ranging in size from ca. 7 Å up to 24 Å (metal-metal edge distance) have been obtained in high yield.

Notably, the compounds here differ from most reported metallocyclophanic compounds in that they lack potentially channel-blocking counter ions (the formal positive charge on each rhenium atom being negated by a coordinated halide). Figure 2 shows, from two perspectives, the X-ray derived single-crystal structure of a small square com-

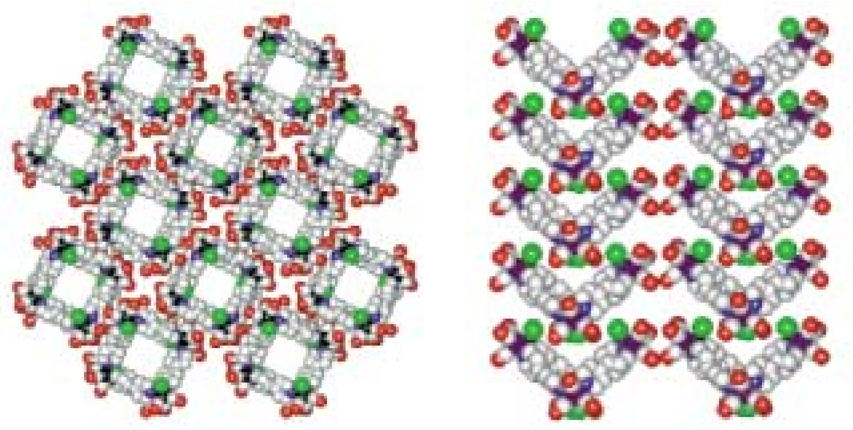


FIG. 2. Space-filled representations of the X-ray crystal structure of and packing arrangement of the 4,4'-bipyridine bridged molecular square. Note the existence of one-dimensional channels, suitable for small-molecule transport. (For clarity, hydrogen atoms have been omitted.)

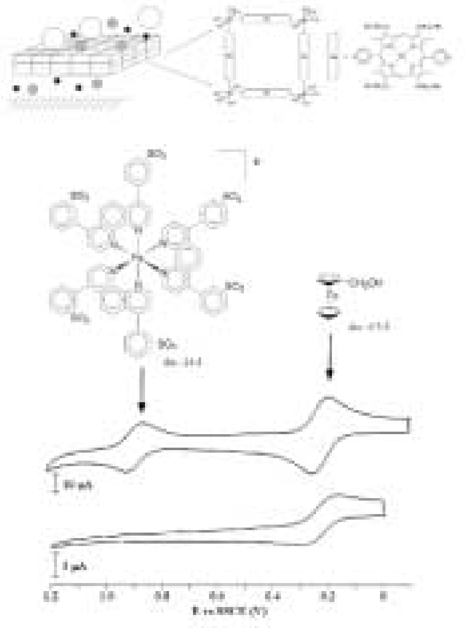
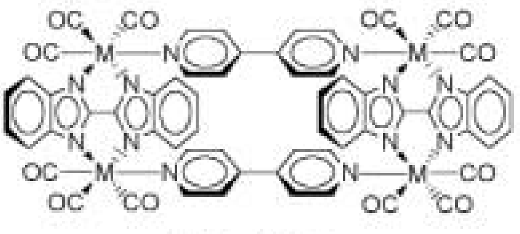


FIG. 3. Electrochemical observation of molecular sieving by a porphyrin-square film. Upper plot shows the voltammetric response of a naked electrode to a solution contain large and small diameter redox species. Lower plot shows the voltammetric response of a film-covered electrode. Note that the larger complex is blocked.



1, M = Mn, Re

FIG. 4. Chemical structure of manganese and rhenium molecular rectangles comprising thin films capable of shape-selective molecular transport.

pound featuring 4,4'-bipyridine ligands as edges. Note the formation of one-dimensional channels. For this compound, the metal-metal separation distance (edge distance) is ca. 11 Å, while the minimum van der Waals cavity diameter (channel diameter) is ca. 8 Å. The structurally determined void volume of the material in Fig. 2 is nearly 50%, while the internal surface area is ca. 40 m^2/g, *i.e.* comparable to many zeolites. In addition to providing open channels, the absence of counter ions renders the molecular materials completely insoluble in water – a desirable property for many sensing and catalysis applications.

Nanostructured Molecular Materials as Molecular Sieves

Thin films of neutral square molecules display size-selective porosity—molecular sieving behavior. The sieving is characterized by sharp molecular size cutoffs where the cutoffs correlate with the known cavity sizes of isolated squares. One way of observing sieving is to use films, mounted on porous supports, as separators at the junction point of a simple U-tube initially containing candidate permeants in only one compartment. The appearance of chromophoric permeants in the receiving compartment can be easily followed by electronic absorption spectroscopy. This approach has been used by Martin and co-workers in their studies of somewhat different nanoscale porous materials: gold-coated channels in track-etched polymeric membranes.[5]

Another approach—one that we have used much more extensively—is to construct films on working-electrode platforms. Redox-active probe molecules that can successfully negotiate the film channels can be observed electrochemically. Figure 3 illustrates the scheme and shows a published example: a small molecule (ferrocenemethanol) permeates a porphyrin-square based film, but a large molecule (a 24 Å diameter bathophenathrolinesulfonate complex of iron(II)) is blocked.[6] Additional studies confirm that discrimination by the neutral molecular film is based on permeant size rather than charge or other properties.

Shape selectivity can be induced by replacing molecular squares with molecular rectangles (Fig. 4) as building blocks for thin films. Probe molecules that are elongated and flat, such as ethylviologen, are readily transported through thin films, while molecules of similar volume but more symmetrical shape are blocked. We suggest that size- and shape-selective molecular transport through materials of this kind will ultimately prove to be of considerable value in membrane-based catalysis, and perhaps also in ultrafiltration-based chemical separations.

Molecular Transport is Fast

A convenient and exceptionally precise way of measuring thin-film molecular transport rates in solution environments is quantitative scanning electrochemical microscopy (SECM). By using micropatterned electrodes as platforms for thin films and by employing the patterned electrodes in a generator mode and the SECM tip in a collector mode, the magnitude of the current from a probe molecule can be used to determine its permeability, *i.e.* the product of the probe molecule's film-based diffusion coefficient and solution-to-film partition coefficient.[7]

SECM and related rotating-disk-voltammetry measurements show that probe molecules typically permeate thin-films of the non-porphyrinic squares 20 to 50 times faster than they permeate amorphous metallo-polymeric films featuring similar molecular size cutoffs. The advantage likely reflects the ordered channel structure of the molecular materials. Porphyrin-based films, which are apparently less well ordered, seem to offer less of a transport advantage.

The materials display classic permeation-type behavior. The molecular flux increases dramatically as the film thickness decreases, reaching exceptionally large values for the thinnest films examined, Fig. 5. High fluxes are important for sensing, catalysis, and especially separations applications.

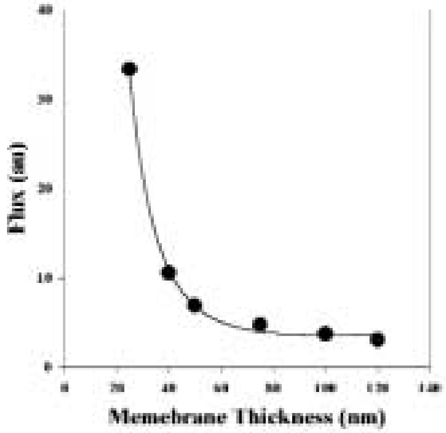


FIG. 5. Transport rates as a function of film thickness. The permeant is Fe(bpy)$^{2+}_3$. The inverse dependence on thickness is characteristic of membrane-diffusion limited transport. For the thinnest film the flux is exceptionally large: For a 100 mM solution of permeant the anticipated flux is roughly 10 moles m^{-2} min^{-1}.

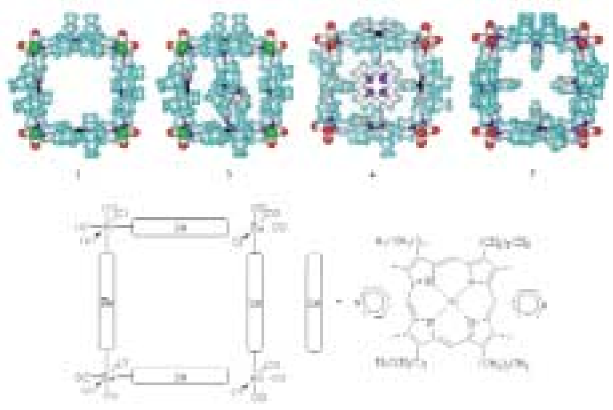


FIG. 6. Top: space-filled representations of molecular structures of an empty porphyrin square (2), and modified squares (3-5) containing, respectively, a difunctional ligand, a tetra-functional ligand, and four mono-functional ligands. The modified squares, when used to construct highly porous thin films, display modified molecular sieving and binding properties. Bottom: diagrammatic chemical structure of an empty porphyrin square molecule, assembly 2.

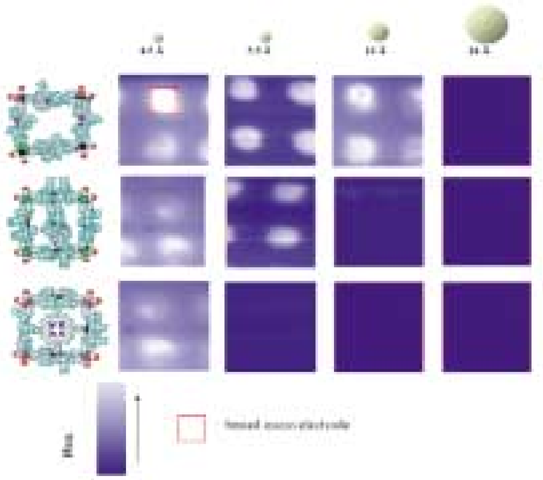


FIG. 7. Scanning electrochemical microscopy images for a series of porous molecular materials (thin films) covering an array of microelectrodes. An SECM image corresponding to the buried microelectrode is expected when the redox probe molecule can permeate the film. A featureless image is indicative of exclusion of the probe molecule. The observed pattern of permeation/exclusion behavior with the series of probe molecules correlates with the behavior anticipated based on transport through the cavities defined by the isolated assemblies, 2-4.

Materials with Chemically Tailored Cavities and Channels

High-porosity porphyrin-containing molecular materials offer channels and cavities that can be functionalized to yield desired shape, size, chirality, and chemical compositional properties. The basis for functionalization is in axial ligation of an otherwise tetra-coordinate metal ion such as Zn(II) located at the center of each porphyrin face. As suggested by the structures in Fig. 6, channel-modifying ligands can be attached to a single wall or to multiple walls. One of the virtues of the channel functionalization approach is that a large number and variety of cavities can be obtained from a single template structure with minimal additional chemical synthetic effort. Indeed, using this approach we have prepared more than 100 variants of the simple square cavity offered by the empty porphyrin assembly 2 of Fig. 6.

As one might expect, chemically tailored channels display molecular transport behavior that differs from empty channels. Most obviously affected by the tailoring are molecular size cutoffs. Figure 7 illustrates some of the differences observed experimentally. Briefly, the figure contains a series of SECM images of thin-film permeation, involving progressively larger redox-probe molecules. As the cavity size of the component square molecule is reduced (via chemical functionalization) the size cutoff for transport is likewise reduced until only very small molecules can pass through the film.

In addition to size selectivity, one could envision channel modifications leading to chemical selectivity, for example, selective hydrophilic versus hydrophobic permeant molecule transport, or selective transport based on permeant charge. Preliminary studies, using supported films, indicate that transport selectivity based on permeant hydrophilicity/hydrophobicity can be engendered via appropriate channel functionalization. Induction of charge-selective transport, however, has not yet been attempted. Nevertheless, based on work by Martin and co-workers, who modified gold nanotubule interiors with charged adsorbates, the idea appears feasible. It should be noted that in other studies involving gold nanotubule structures, Martin's group has successfully demonstrated the concept of hydrophilic/hydrophobic con-

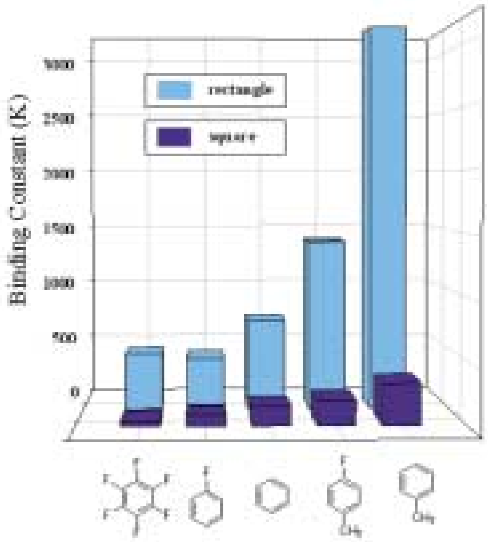


FIG. 8. Binding constants (M^{-1}) for several aromatic guest molecules. Rectangle-based materials, which offer good shape complementarity, bind the planar guests much more strongly than do square-derived materials.

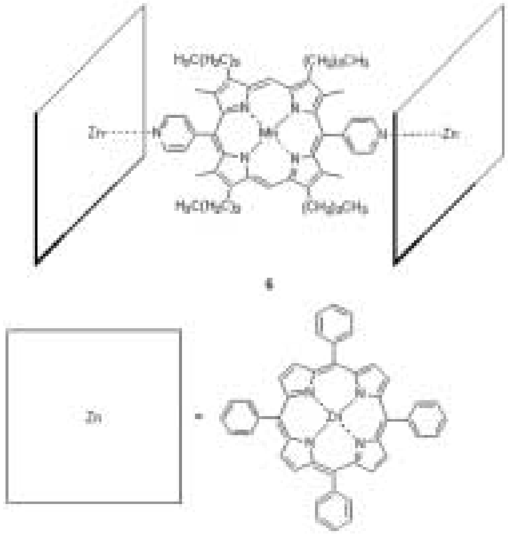


FIG. 9. Schematic representation of a reactive "triad." The central porphyrin is an efficient catalyst for olefin epoxidation. The peripheral porphyrins protect the catalyst from attack by other catalytic centers, thereby extending its lifetime. Squares similarly stabilize catalysts.

trol of nanostructured membrane transport rates.[5]

Nanostructured Molecular Materials and Chemical Sensing

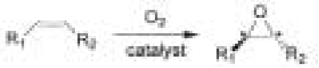
The availability of cavities of molecular dimensions suggests that individual squares could function as hosts for molecular guests and that materials composed of squares or related assemblies could serve as active components of simple chemical sensors. Studies by Keefe and co-workers, using thin films (typically, a few hundred molecular monolayer equivalents) of small or intermediate sized squares as coatings on quartz microcrystals, showed that the materials indeed could be used to sense small, volatile organic compounds such as benzene and toluene.[8] In the studies, advantage was taken of the high porosities of the multilayer materials to obtain much larger gravimetric responses than can be obtained using single monolayers of host molecules. This translates into lower analyte detection limits and wider dynamic ranges for multilayers, given equivalent monolayer versus multilayer host:guest binding constants.

Even simple molecular squares are capable of displaying some elements of selectivity. For example, small cyclophanic squares bind aromatic guests more strongly than aliphatic guests. Also, squares successfully discriminate between candidate guest molecules on the basis of guest size, excessively large guests being excluded from film cavities and channels. Nevertheless, binding constants are small and chemical specificity is poor. One route to stronger binding is to match the host cavity not only to the guest size but also the guest shape. Figure 8 compares the guest-binding ability of a material composed of rectangles with a material composed similarly sized squares.[9] The enhanced host:guest shape complementarity attainable with the rectangle motif leads to substantially stronger binding of planar aromatic guest molecules. It also results in enhanced discrimination between structurally similar guest molecules.

Selectivity can also be induced by functionalizing square cavities with known ionic or molecular receptor groups. One example features an azo-crown type receptor. Squares containing this receptor are capable of selectively binding alkali metal ions. Detection is achieved via photoluminescence: metal ion binding shuts off the known redox quenching behavior of the secondary amine comprising a portion of the crown and permits the porphyrin to fluoresce.

Molecular Assemblies and Chemical Catalysis

High-porosity molecular materials like that depicted in Fig. 2 structurally resemble one-dimensional zeolites. The known catalytic activity of many zeolitic materials raises the question of whether molecular materials might be similarly catalytically active. We find that molecular assemblies comprising the materials indeed can function as selective catalysts, although not in the same way as zeolites. The molecular assemblies are not designed, for example, to withstand the high temperatures and pressures that characterize many zeolite-catalyzed reactions. They are, however, well-suited to high-value-added, ambient temperature reactions occurring in condensed phases. One example is olefin epoxidation (*Reaction 1*), a reaction often used to generate reactive precursors for synthesis of pharmaceuticals and fine chemicals.



(1)

When conventional catalysts such as manganese-porphyrins or –salens are used in Reaction 1, catalysis typically stops after 5 to 50 turnovers. The problem, in part, is attack of the catalyst by other catalyst molecules that have mistaken it for the target reactant. Alternatively, turnover can be terminated when catalysts combine unproductively to form inactive oxo-bridged dimers. The reversible combination of catalyst molecules with bulky end groups, such as zinc porphyrins, results in assemblies such as 6, as shown in Fig 9. These intentionally sterically cumbersome assemblies prevent catalysts from encountering each other and significantly extend catalyst lifetimes. With these in hand it is simple to extend the idea to square-encapsulating catalyst motifs like 3 and 4 shown in Fig. 6. These assemblies have been found to extend epoxidation catalyst lifetimes by up to three orders of magnitude. At the same time, the restricted access provided by the encapsulating square induces size selectivity with respect to candidate reactants. Extension of the catalyst-encapsulation concept to the solid state could yield arrays of extremely long-lived nanoscale reactors capable of chemically processing appropriate target molecules even as they selectively sieve and separate the molecules from undesired compounds.

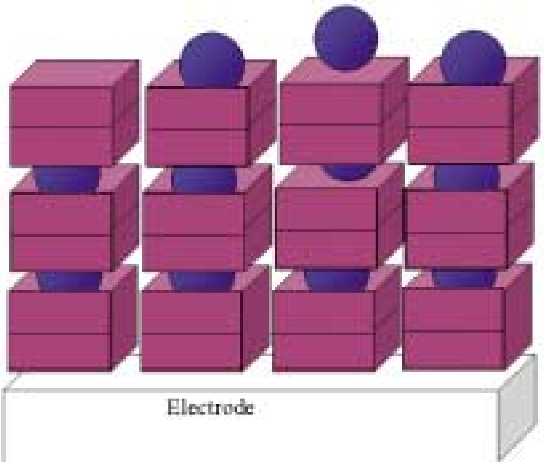


*FIG. 10. Schematic representation of a nanocomposite material prepared by physical encapsulation of functional entities (spheres) by pentaporphyrin boxes (*e.g. *species 3 or 4).*

Advanced Molecular Materials

With these first- and second-generation materials in hand, and with their structural and functional properties reasonably well characterized, advanced materials are now emerging, with development occurring mainly along three lines. The first centers on polypeptides. These are incorporated within square cavities via carboxylate/tin(IV)porphyrin chemistry. The notion is to convert existing high-porosity, sensor-compatible molecular materials into materials that are exceptionally selective for uptake of specific heavy metal ions and for recognition of small biomolecules.

The second line of development takes advantage of the encapsulating properties of aggregates of cavity-derivatized squares such as assemblies 3 and 4 in Fig. 6, to generate nanocomposites. The approach is illustrated in Fig. 10. Components that are small enough to fit within a molecular-square cavity, but too large to escape through the ports of the cavity, can be encapsulated in stoichiometric fashion. For example, assembly 3 in Fig. 10, which features an 18 Å diameter cavity, efficiently physically encapsulates a ca. 16 Å diameter coordination complex, permitting the resulting film-immobilized collection of complexes to be addressed electrochemically. Among other things, this suggests electrocatalysis applications for molecular nanocomposites. Although they have yet to be examined, one could also easily envision nanocomposites featuring physical encapsulation of small dendrimers (see the article in this issue by Crooks) or small metal particles (see the article in this issue by Feldheim), and displaying unique physical or chemical properties. Beyond providing a novel way of organizing chemically and functionally interesting entities such as dendrimers or nanoparticles, the chief attraction of the encapsulation/nanocomposite-formation strategy is that new materials can be obtained without expending synthesis effort to develop attachment or binding chemistry.

The third line of development is a departure from the theme of purely molecular materials. By chemically functionalizing porphyrinic squares with appropriate reactive groups—for example, hydroxyl groups—and then combining these with chemical linkers featuring complementary functional groups, polymers of squares can be generated. When the polymerization is carried out at a liquid/liquid interface, polymer growth is self-limiting and thin films are obtained. In contrast to molecular films, the polymeric films are flexible and are stable in polar organic solvents. We anticipate that the enhanced mechanical and chemical stability of the polymeric materials will prove useful in a number of functional applications, including variants of the applications described above. ■

Acknowledgments

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