

spondences and borrowings still remains.

If words hit a time barrier when it comes to detecting linguistic links, must the deep links between languages and cultures remain forever obscured? Linguists such as Nichols (4) have argued that language structure holds the key to unlocking our past. By examining structural features such as the position of verbs in clauses and the presence or absence of inclusive/exclusive pronominal contrasts, Nichols claims to recognize linguistic areas and connections that are beyond the reach of the traditional comparative method with its focus on vocabulary. Although this approach appears promising, not all linguists are convinced that the structural features used by Nichols are any more stable than words. Campbell (5), for example, cites cases of recently diverged dialects that differ in features that are allegedly stable for periods of more than 10,000 years.

On page 2072 of this issue, Dunn *et al.* (6) tackle this debate in a systematic and rigorous manner, using methods derived from evolutionary biology. As Darwin noted (7), languages evolve in remarkably similar ways to biological species. They split into new languages, mutate, and sometimes go extinct. There are numerous historical connections between biology and historical linguistics, with linguistics often leading the way in the development of new ideas and methods (8). However, despite these connections, linguists have not commonly used the phylogenetic methods that have revolutionized evolutionary biology in the past 20 years [for recent exceptions, see (9–11)]. To address the problem of detecting deep signal, Dunn *et al.* borrowed two tools from their biological colleagues. First, they constructed a database of 125 structural features for 16 Austronesian and 15 Papuan languages. This enables them to avoid the charge that they merely selected a few features that happened to fit their hypotheses. The number of possible family trees of descent for even quite small numbers of languages is vast. Dunn *et al.*'s second methodological borrowing from biology was the use of a computer program to find the set of optimal trees for the Austronesian and Papuan data sets. To test whether the structural features contain a historical signal, Dunn *et al.* compared the Austronesian structure tree with the traditional classification of these languages. The resulting Austronesian structure tree matched the traditional classification quite well, which suggests that the structural features contained some historical link or signal for at least the 4000-year time depth that the Austronesian of languages studied by Dunn *et al.* are thought to have.

What about time depths beyond the reach of traditional methods? Evolutionary trees

show nested patterns of descent, with the most recent divergences toward the branch tips and the most ancient at the tree base or root. The Papuan tree of Dunn *et al.* shows some geographic clustering at its tips. The signal toward the base of the tree is very weak, suggesting that few structural features support these historical links. However, the signal that is present is consistent with a scenario involving a time depth greater than 10,000 years. Dunn *et al.* are careful to emphasize that the signal is weak and discuss alternative hypotheses. Although it does not conclusively demonstrate deep historical signals in structural features, the Dunn *et al.* paper sets new standards for the systematic collection and analysis of structural features. Its approach is likely to be widely emulated by researchers working on languages in other regions. In the future we may see the development of Web-based databases for the languages of the world similar to the GenBank repository for DNA sequences. The task of making accurate inferences about our past is a demanding one that requires the integration and triangulation of inferences from genetic, linguistic,

and archaeological data (12). The Dunn *et al.* approach is an important step forward in this interdisciplinary endeavor.

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#### CHEMISTRY

## Better Living Through Nanopore Chemistry

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**T**iny holes have huge significance—at least if you're in the business of cracking millions of barrels of crude oil into useful smaller chemical components, converting methanol into gasoline, or transforming toluene into precursors for polymers. Zeolites, the remarkable materials that catalyze these conversions, contain enormous numbers of cavities of roughly nanometer size (1). The cavities are uniform in size and shape and are interconnected to form extended channels or pores. The cavities and the portals between them are just the right size to imbibe oil's molecular components and process them into more useful and valuable petrochemicals.

Zeolites are mostly made from the elements of Earth's crust: silicon, aluminum, and oxygen. This makes for strong materi-

als—in essence nanoporous rocks. But this chemical composition constrains the possible applications of these materials. For example, an important problem in chemical catalysis, especially in the area of pharmaceuticals, is the transformation of an achiral reactant selectively into just one of two possible mirror-image products (“enantioselective” catalysis). Yet purely zeolitic schemes for enantioselective catalysis are rarely, if ever, encountered.

What if the most promiscuous of elements—carbon—could be recruited for assembling zeolite-like materials? The versatility and variety of carbon chemistry—the chemistry of life—could, in principle, expand tremendously the range of compositions, architectures, and functional behavior of permanently porous crystalline materials. On page 2040 in this issue, Férey and co-workers report the latest in a series of advances in this area (2). The new material, called MIL-101 (where MIL stands for Matériaux de l'Institut Lavoisier), has some remarkable physical attributes. The unit cell volume is ~700,000 cubic angstroms, about 90% of it empty space once volatile solvent

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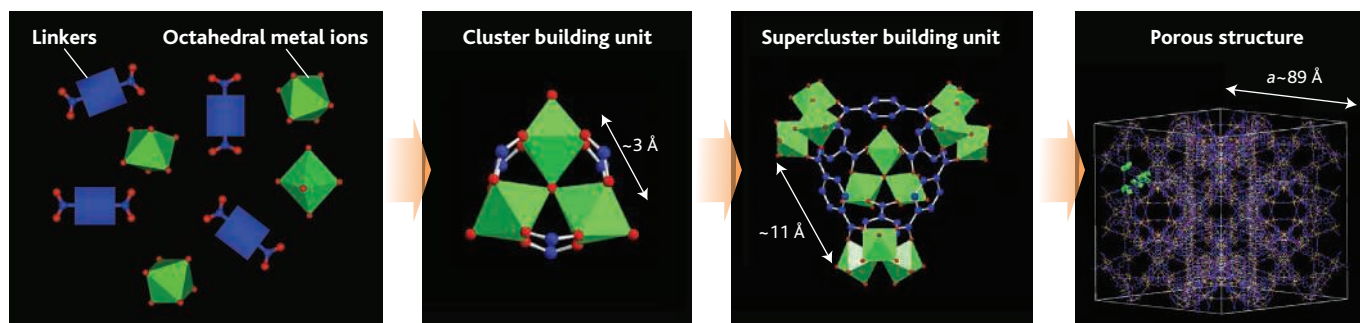
molecules are removed. The estimated internal surface area is  $\sim 6000 \text{ m}^2/\text{g}$ . A tablespoon of MIL-101 has the surface area of a half-dozen football fields, or about seven times the area of the most catalytically effective zeolites.

As elegant as the new material is, the more important questions are “how did they do it?” and “what makes it so difficult?” The notion of enlisting organic chemistry to make new stable and highly ordered porous materials is the focus of scores of research groups around the world. A common

then scaling up the size of the building units may produce large pores. For example, in place of single metal ions or small clusters, the key building unit for MIL-101 is a supercluster consisting of four smaller clusters (stabilized  $\text{Cr}_3\text{O}$  units) linked by difunctional organic components to make a large tetrahedron. Besides increasing the scale, the supercluster presents a larger number of organic ligand attachment points (chelating sites) than does either a small cluster or a single metal ion. Furthermore, the sites are oriented differently on the

as possible. They then rank the structures according to energetic stability, again computationally. Finally, they examine the handful of low-energy structures, calculate powder patterns, and look for a match to the experimental pattern. The ranking strategy works because the “solvothermal” conditions used in the synthesis generally produce thermodynamic rather than kinetic structures.

Are hybrid materials with even larger pores and more complex structures on the horizon? Probably, but the more important



**Big results from small holes.** Starting from simple assemblies and linking units, larger and larger building blocks combine to form crystalline nanoporous materials with more surface area than zeolites.

approach is to retain some of the inorganic character of zeolites (although not necessarily with the same elements) and build hybrid organic/inorganic materials. The approach works well, at least if the cavities and pores are small. Unfortunately, as the targeted cavities get larger (diameters beyond a nanometer or so), success becomes increasingly rare. Instead, the pores collapse, duplicate frameworks interpenetrate and fill the pores, or, most exasperating of all, some version of the desired porous material is indeed obtained, but the detailed structure is so complex that it cannot be determined from conventional measurements.

To work around these problems, Férey and co-workers make use of three ideas. First, the chances of success increase if discrete multi-atom building units can be designed and generated in the solution phase (see the figures). Powerful examples, most notably from the work of Yaghi *et al.*, are framework vertices comprising metal-oxo clusters (3). They present the right number of organic ligand attachment sites, in the right orientation, to yield networks defining porous hybrid structures.

Second, if small pores can be obtained,

supercluster surface than on smaller clusters, implying that different framework structures can ultimately be expected.

The third idea has to do with determining the structure of the new hybrid material. Usually this is done by transforming structural data that have been generated in inverse space by diffraction of x-rays by single crystals. However, as unit cells get larger, the chances of growing highly diffracting single crystals get smaller, a problem well known in determining protein

structures. Valuable information about structure, again in inverse space, can be obtained from powder x-ray measurements (diffraction by many randomly oriented microcrystals). Owing to the reduced information content of the powder measurement, determining the structure in real space is a demanding problem unless one already has guessed a reasonable model structure as an analysis starting point. This is not so difficult if the possibilities are

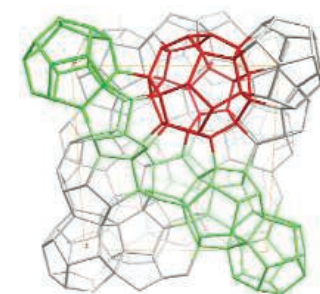
few. But for complex materials like MIL-101 the number of possibilities is staggering. Férey *et al.* (2) reduce the possibilities by using a computational assembly algorithm to find as many candidate structures

goal may be to incorporate useful function. Férey *et al.* allude to this, describing briefly the compartmentalized uptake of redox-active guests and the use of MIL-101 as a mold for fabricating nanostructured semiconductors. If unusual optical, magnetic, and electronic behavior can be introduced, interesting applications in chemical sensing and energy conversion will follow. Important for seeing such behavior is the introduction of new kinds of building units—ones where function is on an equal footing with structure. One interesting example is Halper and Cohen’s use of large chromophoric coordination complexes as building units, although permanent porosity for the resulting materials has yet to be reported (4).

Finally, what about zeolite-like catalysis? Hybrid materials lack the thermal stability to replace inorganic ones in these high-temperature processes. More important will be higher value transformations under milder conditions. Particularly exciting is a new report by Lin and co-workers of enantioselective catalysis (5) that tackles just this challenge.

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**Cagey structures.** Zeotype architecture of MIL-101 showing mesoporous cages with diameters of 29 Å (green) and 34 Å (red), featuring 12 Å pentagonal and 15 Å hexagonal openings [adapted from (2)].