Shaping Synthetic Metals

Dendrimers branch out into the electronic world

By CORINNA WU

It's not difficult to think of dendrimers as organic molecules. After all, diagrams of their structure look organic—a spherical star burst of floppy branches resembling a sea creature. Many scientists are excited about the prospect of developing dendrimers with electrical and optical properties because, like other polymers, dendrimers are flexible, lightweight, and easy to fabricate.

One thing sets them apart, though, says Donald A. Tomalia of the Michigan Molecular Institute in Midland: "They conduct electrons in all three directions, and that's totally unlike any other organic [polymer]."

Tomalia, who developed the concept of making dendrimers more than 2 decades ago (SN: 1/13/96, p. 31), views them as "artificial metals," with the spherical molecules acting as the much smaller metal atoms do. Dendrimers provide an added benefit: Scientists can alter the size and chemical composition of the molecules, an ability that allows them to go beyond mixing and matching individual elements from the periodic table.

Tomalia says he has always suspected that dendrimers could behave like versatile analogs of atoms, and now they are beginning to fulfill that promise. Two years ago, he, along with Larry L. Miller of the University of Minnesota in Minneapolis and their colleagues, synthesized the first electricity-conducting dendrimers. Recent work hints that dendrimers functioning as magnets, light-emitting diodes, liquid crystals, lasers, and antennas are not far behind.

Much of the value of dendrimers comes from the chemist's ability to precisely control their architecture during synthesis. Most polymers are made by repeatedly connecting small building blocks into long chains. After the initial reaction starts, the polymerization process continues to add the same subunits. Stopping the reaction at a certain time produces polymers that fall within an often wide range of molecular sizes.

In contrast, scientists have many ways of controlling the shape and size of dendrimers. They can choose the core molecule, the length and chemical composition of the branches, and the number of layers they add.

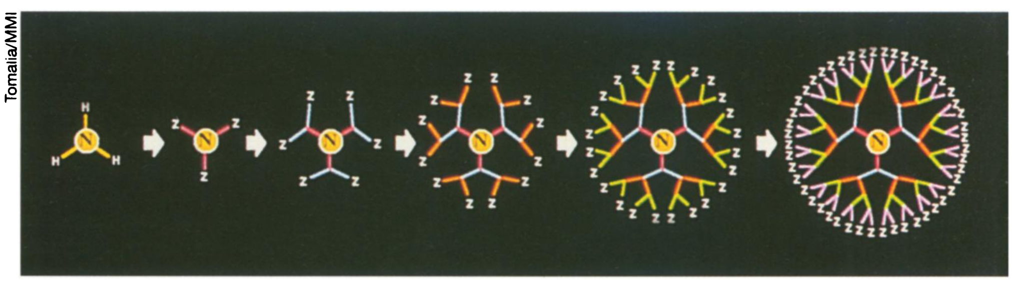
In one approach, called divergent synthesis, researchers start by attaching branches to a core molecule. Subsequent steps add more branches on top of existing ones—like making a papier-mâché sculpture.

A second method, called convergent synthesis, forms the intricate branches first, then connects them to the core molecule. Both approaches result in fractal molecules, compounds that look the same up close as they do from a distance (SN: 1/23/93, p. 53).

Miller says. "Nevertheless, the conductivity can be quite high." The researchers analyzed the compound in the Feb. 5 Journal of the American Chemical Society.

That dendrimer film conducts better than any other polymer of its kind that's stable in air. Another polymer, polyacetylene treated with sodium naphthalide, conducts more than four times the electricity but breaks down when exposed to air. Still, Tomalia says, "we have a long way to go to match the conductance of copper."

He notes that this molecule is one combination of 50 known dendrimer families and 150 possible surface modifications, so "there will be many others that will give exciting and unique properties."



To form a three-dimensional dendrimer, chemists attach multiple layers of branches to a core molecule. By controlling the direction in which the branches grow, they can create dendrimers with a variety of shapes.

To conduct current, a dendrimer's branches must have a network of double bonds, a property chemists call conjugation. In linear conjugated polymers, such as polyacetylene and polyaniline, electrons run along a single chain and then hop over to the next one, Miller says.

The branching in dendrimers introduces a third dimension to electric conduction. "The conductivity is really isotropic," says Miller. "It's the same in all three directions." In that regard, dendrimers have a counterpart in buckyballs, the 60-carbon molecules shaped like a soccer ball (SN: 8/24/91, p. 120). Buckyballs also conduct in three dimensions, but they are not as easily modified chemically as dendrimers.

The conducting dendrimers synthesized by Miller and Tomalia have branches of the polymer polyamidoamine with negatively charged diimide ions attached to the outer surface. Only the diimide passes electrons along, so "the amount of conductor in there is pretty small,"

One important factor that affects how well the dendrimers conduct electricity is their ability to form high-quality films that don't crack or crumble. The chemists had some difficulty, Miller says, but they eventually found conditions that worked. If the outermost branches of each dendrimer are too dense, the molecules don't interlock well with each other.

An unexpected property of the dendrimer films suggested another application. One day when Miller's colleague Robert G. Duan was studying the dendrimers, he noticed that the conductivity was moving up and down in time with his breathing. He then blew on the film and saw the conductivity jump dramatically. It turned out that the changes were caused by water vapor. An increase in humidity from zero to 90 percent causes a 500-fold increase in conductivity.

The researchers don't know for sure why this happens, but they suspect that the water vapor reacts with the dendrimer molecules, sticking them together. "It improves the contact between these anion radical conductors and makes a better network for conductivity," Miller says. Because the reaction is reversible, dendrimers could possibly be used in sensors for water vapor or other gases.

Good films will also be essential for dendrimer light-emitting diodes, or LEDs, devices that give off light in response to electricity. Miller and his colleagues have made some LEDs out of a different dendritic polymer and are currently preparing to test them. A group led by Jean Fréchet of the University of California, Berkeley has also made significant progress in developing dendrimer LEDs that emit white light.

In some cases, what's desirable about dendrimers is not their ability to connect but their ability to isolate. Like buckyballs, dendrimers can act as containers for other atoms, giving them different properties by providing them with an outer coat. Buckyballs, however, have a fixed size of around 10 nanometers, whereas dendrimers typically start at that size and go up, Tomalia says.

His colleague at the molecular institute, Lajos Balogh, has placed clusters of iron, cobalt, and nickel atoms inside polyamidoamine dendrimers, creating tiny magnets. Working with the National Institute of Standards and Technology, they've verified that the dendrimer magnets don't show any hysteresis; that is, the material's magnetic properties don't change when a magnetic field is applied repeatedly to it. The team is currently applying for a patent on the dendrimer magnets.

The researchers fill the dendrimers with soluble metal ions, which bind to chemical groups inside the molecule. Then, the scientists add electrons to the ions, turning them into insoluble metal and effectively trapping them inside. Tomalia, taking a cue from his son, calls this the "Winnie-the-Pooh effect," referring to the A.A. Milne story in which the bear got stuck in a friend's doorway after a particularly large lunch.

Normally insoluble materials such as semiconductors and metal sulfides can dissolve in solution once they're wrapped in a water-soluble dendrimer. That suggests potential biological applications, Tomalia says, such as new ways to deliver drugs. Dendrimers with branches designed to bind to tumor cells could be loaded with radioactive ions to deliver a therapeutic dose of radiation (SN: 2/22/97, p. 117).

The cargo space and number of chemical groups inside the dendrimer govern the size of the metal clusters included. Thus, dendrimers could act as molds for quantum dots, tiny clusters of material whose properties differ from those of large amounts of the same material (SN: 4/4/92, p. 222). Also, rod-shaped dendrimers, which can reach up to 600 nanometers in length, could hold copper and serve as molecular wires, Tomalia suggests.

Fréchet and his colleagues are placing rare-earth elements such as erbium inside dendrimers for use in the telecommunications industry. In fiber-optic cables, light loses some of its intensity as it travels along, so telephone companies install amplifiers every mile or so to boost the signal. The amplifiers consist of coils of cable doped with erbium, Fréchet says. Erbium absorbs the incoming light and emits it at a wavelength that travels well through the material.

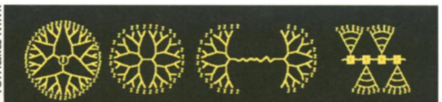
The emitted light tends to be dissipated by other, nearby erbium ions, however. One solution, says Fréchet, is "to make sure an atom never touches another by wrapping it in a dendrimer."

Using the convergent synthesis approach, the researchers attach a positively charged erbium ion to three negatively charged polyether branches. The outside of the dendrimer is made to be compatible with the fiber. Fréchet plans to present this work in September at a meeting of the American Chemical Society in Las Vegas.

Optical properties often go hand in hand with electrical properties, Miller says. Recent work by Jeffrey S. Moore of the University of Illinois at Urbana-Champaign and Raoul Kopelman of the University of Michigan in Ann Arbor demonstrate that small dendrimers can be made to collect and focus light, like nanoscopic antennas. They described their findings in the Feb. 17 PHYSICAL REVIEW LETTERS.

Because of their structure, dendrimers are "almost perfect antenna molecules," says Moore. Many light-collecting chemical groups on the outside funnel signals to a light-emitting core. Moore and his colleagues tested two groups of phenylacetylene dendrimers that had similar geometry but different sizes and shapes. Both groups included dendrimers with three branches emanating from a central benzene ring; a difference in the branches made one group's molecules globular and the other's larger and flatter.

The researchers aimed photons at the dendrimers and counted the number absorbed by the outside layer and the number emitted from the core. They found that in the globular dendrimers, light often traveled from the center to the periphery. This result made sense, Kopelman says, because there are "twice as many [pathways] going out as there are going in."


Tomalia/MMI

Dendrimers in the shape of a sphere, ellipsoid, fan, and rod (left to right).

The large, flat dendrimers, however, turned out to have a built-in energy funnel that helped improve the efficiency of light collection. This energy funnel—an increased number of rings in a linear chain deep in the molecules—guided electronic excitations from the outer surface to the core. With no energy gradient built in, "the actual efficiency drops off after the fourth generation," or layer of branches, Moore says.

The brightest dendrimers tested so far—that is, those emitting the most light from the core—have about 127 collecting groups on the outside, with efficiencies of nearly 99 percent.

The solvent seems to exert a "dramatic influence" on the electron transfer properties of large dendrimers, an unusual response that the researchers do not fully understand, Moore says. Dendrimers react to light very differently when dissolved in pentane rather than hexane, for example. Different solvents may cause the outer branches to fold back, he suggests, moving closer to the core and providing a shortcut through space for the electrons.

The solvent effect could be exploited for another application—octane sensors for gasoline, Moore notes. Gasoline contains a mix of hydrocarbon chains of various lengths, and it's ordinarily difficult to distinguish between these closely related compounds when they are commingled. Perhaps by dissolving dendrimers in a gasoline sample and analyzing the resulting light absorption, the proportions of hydrocarbons could be easily determined.

Tiny antenna molecules could also serve as ultrasmall light sources for high-resolution microscopy, Kopelman says, or as more efficient collectors for processes that mimic photosynthesis. Even photosynthetic proteins harvest just one photon at a time and convert it into chemical energy. A dendrimer with a reactive core could transform a large number of photons collected at one time into useful energy to jump-start chemical reactions. Using dendrimers to concentrate light also foreshadows organic lasers, Fréchet notes.

Moore and his colleagues are already pursuing another line of investigation—dendrimers as liquid crystals. "People thought they were amorphous," he says. "We're learning how to control the state of order." They use disk-shaped dendrimers that stack up in response to an electric field. If these aggregates can conduct electricity, they could provide yet another way for dendrimers to form molecular wires.

Given the many dendrimer variations possible, the field is as intricate and diverse as the molecules themselves. "We're just beginning to tap into this new paradigm," Tomalia says. "Given time, we should see some substantial improvements. We don't know all the rules yet." □