Chemistry

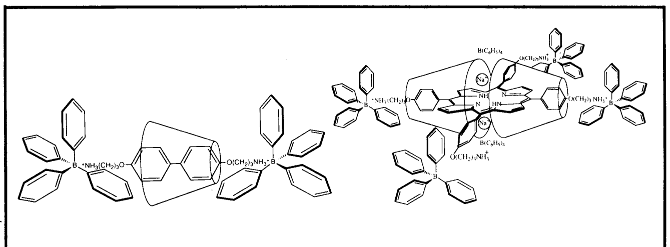
Making molecules that self-assemble

Filling a bag with toy car parts — little chassis, wheels, windows, engines and seats — and then shaking it up yields a bag of jumbled car parts. Imagine the possibilities if the parts could actually find each other, arrange themselves properly and then self-assemble into little cars.

Though self-assembling vehicles remain fantasy, chemists at the State University of New York at Buffalo have carefully designed molecular subunits that automatically snap together into a "threaded molecular loop" and into more complex, oxygen-binding assemblies that the scientists hope to develop into the basis for artificial blood.

"The self-assembly process is a theme found throughout biology," notes project leader David S. Lawrence. In nature, enzymes, organs and even entire human beings self-assemble from smaller constituents. "It's a neat process in which all of the pieces find another, like a jigsaw puzzle coming together giving the correct picture."

In the April 25 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Lawrence and Tata Venkata S. Rao report making a four-piece, self-assembling complex. A long, flat molecule — a diammonium salt with a central, hydrophobic (water-avoiding) region flanked by charged ammonium groups — serves as a template for the complex. One end of the salt threads through the interior of a starch-like molecule called a cyclodextrin, which looks like an empty lampshade, until its hydrophobic center finds itself inside the molecular lampshade. A boron-centered molecule that looks like a four-bladed wing nut then caps each of the salt's two ends.



Lawrence et al./JACS

Four-part threaded molecular loop (left) and a more complicated, 11-piece assembly.

In the March 14 issue of the same journal, Lawrence and John S. Manka report pulling off an 11-piece self-assembly effort. They used a pair of cyclodextrins, six of the wing-nut molecules, a couple of sodium atoms and a square porphyrin molecule with one ammonium-tipped group jutting from each of its four sides. Two of these groups thread through their own cyclodextrin lampshades. The other two sneak sideways through a groove formed by the two bottom-to-bottom lampshades. A wing-nut molecule sticks to each of the four ammoniums. Charged sodium ions hover above and below the plane of the porphyrin, and a wing nut associates with each of these as well. In all, 11 pieces come together to make the complex.

Lawrence told SCIENCE NEWS he has also made complexes with cobalt-centered porphyrins. Like the iron-centered porphyrin (heme) molecules in the blood protein known as hemoglobin, these complexes bind oxygen. With further development, such complexes might serve in artificial blood formulations, Lawrence says.

He points out that none of the parts of these assemblies link up via covalent chemical bonds, which connect the atoms that make up the individual pieces. Rather, by timing the addition of successive pieces, the researchers rely on hydrophobic and electrostatic interactions to get the pieces to stick together in just the right way.

Earth Sciences

Why polar bears may follow the sunspots

Most scientists cringe at suggestions that the 11-year sunspot cycle might influence bizarre factors on Earth, such as the number of polar bears hunted down each year. But a new study adds an intriguing twist to the polar bear proposal. Two researchers report finding a statistical link between the sunspot cycle and the severity of winter sea-ice near Newfoundland since the 1920s.

In some years, southerly winds blow an abnormal amount of Arctic sea-ice southward to Newfoundland, causing problems for shipping, fishing and oil-drilling efforts in the area. In other years, the ice is much less severe. Brian T. Hill and Stephen J. Jones of the Institute for Marine Dynamics in St. John's, Newfoundland, say their statistical studies of sea-ice records suggest that such variations follow the solar cycle — a small waxing and waning of the sun's energy output, with an average period of about 11 years. They describe their findings in the April 15 JOURNAL OF GEOPHYSICAL RESEARCH.

The statistical link between ice and solar cycle appears strongest, they say, when the calculations take into account another factor called the quasi-biennial oscillation (QBO) — a pattern of stratospheric winds circling Earth's tropics and reversing direction about every 1 to 1½ years. The researchers found the best match between ice severity and solar variations during years when the stratospheric winds blew from the west. In the last three years, several scientists have described similar statistical links between the solar cycle and Earth's weather patterns during the westerly phase of the QBO (SN: 5/14/88, p.310).

Hill and Jones suggest that periods of strong solar activity could somehow set up patterns of high air pressure that keep sea-ice from blowing south toward Newfoundland. If so, the polar bear link could make some sense, Hill speculates, because years of mild sea-ice might restrict the bears' travels.

Statistical correlations between solar cycle and variations on Earth, while tantalizing, remain quite controversial. Meteorologists can't currently explain how minute changes in the sun's radiation could cause such large variations in Earth's weather.

Coral tells of wetter times in desert

While rain is rare in the Sinai desert these days, an analysis of fossil coral indicates the region was much wetter 100,000 years ago, Israeli and Australian researchers report in the May 10 NATURE.

R. Klein of Tel Aviv University and his colleagues studied terraces of ancient coral reefs along the shores of the Red Sea. Analysis of the corals revealed about 15 to 25 times the concentration of humic acid found in modern coral from the Red Sea. Humic acid is a chemical that comes from organic material in soils.

The fossil reefs grew during geologically brief interglacial periods separating the most recent ice ages. To explain the high humic acid concentrations, the researchers propose the Sinai received much more rainfall during previous interglacial periods than it does today. The rain would have washed humic acid into the sea, where it would enter the bodies of growing coral.

Klein and his co-workers believe they can even pinpoint the time of year when the rains fell. Viewed under an ultraviolet light, the fossil coral shows distinct fluorescent bands with high humic content alternating with nonfluorescent bands with lower humic content. Comparisons with modern coral indicate the fluorescent bands correspond to summer growth, which means the Sinai had a summer rainy season. Similar analyses of fossil coral could help reveal the climate history of other regions around the globe, the researchers say.

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