numbers are likely to dominate at relatively small sizes (*20*).

Our results also allow us to examine the development of the liquidlike state in clusters. The similarity of the radial distribution functions for the bulk and the cluster liquidlike minima (Fig. 3) shows that bulklike liquid structure develops at rather small cluster sizes. The only significant difference is the uniformly smaller value of the cluster radial distribution function, and this is simply due to the finite size. This similarity can easily be understood within the polytetrahedral model of liquid structure. Small clusters bound by medium-range forces have icosahedral growth sequences (*21*). For very small sizes (up to 31 atoms for the Lennard-Jones potential), the lowest energy sequence is purely polytetrahedral, although some close-packed character has developed by the time the 55-atom Mackay icosahedron is reached. Given the favorability of polytetrahedral structure for small clusters, it is not surprising that bulklike liquid character is seen at small sizes.

Similarly, the decreasing polytetrahedral character and increasing close-packed character of the Mackay icosahedron as the size increases can explain some of the differences in the correlation diagrams of the two clusters (Fig. 2, B and C). For the 55-atom cluster, the distinction between the top of the band of defective icosahedral structures and the band of liquidlike minima is unclear because of the relative structural similarity of the solid and the liquid at this small size. The energetic separation of these two bands of minima becomes larger as the size increases, giving the correlation diagrams the two-state character expected for a system that undergoes a first-order phase transition.

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# Reversible Encapsulation of Disc-Shaped Guests by a Synthetic, Self-Assembled Host

Robert M. Grotzfeld, Neil Branda, Julius Rebek Jr.*

Here, the synthesis of a bowl-shaped molecule is described and evidence of its reversible dimerization by means of hydrogen bonds is presented. The dimer features a flattened spherical cavity of peculiar symmetry and acts as a host for the encapsulation of guest molecules of complementary shape. Encapsulation of aromatic guests in chloroform solution and of cyclohexane in *p*-xylene solution was demonstrated by nuclear magnetic resonance experiments. The passage of guests into and out of the cavity is slow and occurs on a time scale of hours. The system was used to explore the effects of size, shape, and solvation on molecular recognition coupled with assembly.

Previous efforts in the synthesis of self-assembled molecular capsules have led to small cavities capable of sequestering methane (*1*) and large cavities that can accommodate molecules of the size of adamantanes (*2*). These earlier capsules present roughly spherical interiors, and their recognition properties reflect preferences for guests of this shape. Here, we introduce an assembly of intermediate size and unusual ($D_{3d}$) symmetry. The overall shape resembles that of a jelly doughnut, and it features a flattened spherical interior cavity. This assembly encapsulates disc-like molecules—for example, benzene or cyclohexane.

As in earlier designs, the assembly involves the reversible dimerization of self-complementary monomers. These associate by interlocking the concave and convex parts of the two monomers and are held together by weak intermolecular forces. The new architectural features are presented schematically in Fig. 1, wherein the threefold symmetry of the monomers is emphasized and the curvature of the dimeric assembly is exaggerated.

The driving force for assembly takes advantage of modest directional characteristics of hydrogen bonds. These are common to many other studies of self-assembly (*3*), and we have found that glycoluril units (for example, **4** in Fig. 2) provide a particularly rich source of donor and acceptor functions desirable for self-complementary structures (*1*). Any number of rigid aromatic nuclei can act as spacers between the glycoluril units; the spacer determines the dimensions and shape of the molecular assembly (*4*). A triphenylene derivative (**2**) was chosen as the spacer, so that the ceiling and floor of the assembled capsule consisted of aromatic $\pi$ surfaces. The fusion of three glycoluril units to the spacer with an all-cis stereochemistry (as in **5**) imparts a curvature to the structure and forces the association to occur in only one way; the maximum number of hydrogen bonds (12) can be achieved only when two molecules present their concave faces to each other.

The synthesis began with the reaction of bromofluoroxylene **1** with magnesium to give hexamethyltriphenylene **2**, in what is formally a benzyne trimerization. Bromination of **2** gave hexakis(bromomethyl)triphenylene **3**, which was used without purification in the alkylation of glycoluril **4**.

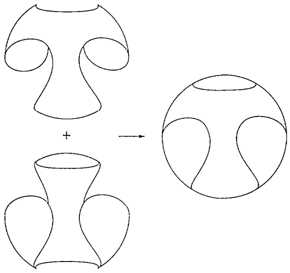

**Fig. 1.** Dimerization of a self-complementary structure to a closed-shell surface.

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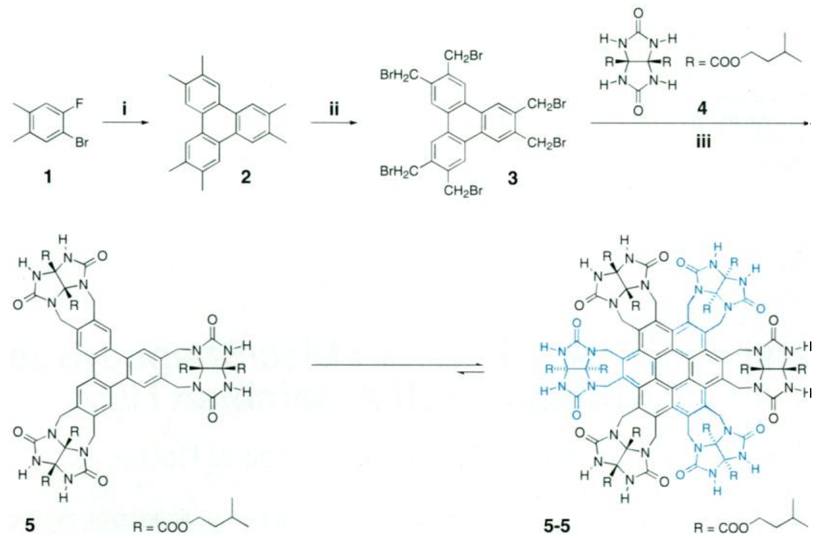

**Fig. 2.** Synthesis of the self-assembling monomer **5**. Bromofluoroxylene **1** was obtained by bromination of fluoroxylene that had been prepared in analogy to fluorobenzene (*8*). Cyclization **i** (Mg, tetrahydrofuran, reflux) was carried out by a modification of a published procedure (*9*). Bromination **ii** ($Br_2$, 1,2-dibromoethane, reflux, irradiation by tungsten lamp) was followed by alkylation **iii** (**4**, dimethyl sulfoxide, *tert*-$BuO^-K^+$, 30°C) of the di-isoamylester-glycoluril **4**, which was obtained as described earlier for the corresponding diethylester derivative (*10*).

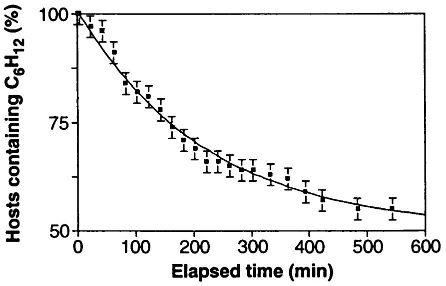

**Fig. 5.** To a solution of 4 μl of cyclohexane (9.3 μmol) and 3 mg of **5** (2.1 μmol) in 700 μl of *p*-xylene-$d_{10}$ was given 4 μl (9.3 mmol) of cyclohexane-$d_{12}$. The solution contained about 5 μmol of tetramethylsilane (TMS), which was used as an internal integration standard. The peak ratio of the encapsulated cyclohexane-$h_{12}$ versus TMS was monitored over time; the remaining hosts encapsulated $C_6D_{12}$. Error bars indicate an estimated 5% experimental error.

Separation of the stereoisomeric products through column chromatography gave the target structure 5.

In organic media, two molecules of 5 associate to form 5-5, a dimer of $D_{3d}$ symmetry. Spectroscopic features indicate that the dimer is held together by 12 strong hydrogen bonds. The $^1H$ nuclear magnetic resonance (NMR) spectrum of 5-5 in $CDCl_3$ shows characteristically downfield resonances at 8.96 ppm for the N-H protons; these signals are independent of concentration. The infrared spectrum shows the N-H stretching absorption appearing at 3214 $cm^{-1}$. Upon addition of benzene-$d_6$ to a solution of 5-5 in $CDCl_3$, a second set of signals appears in the $^1H$ NMR spectrum, indicating the presence of a new species. Titration experiments with benzene in $CDCl_3$ reveal that the concentration of the new complex increases in a linear fashion with benzene concentration. For example, in $CDCl_3$ with 14 volume % benzene, about one-third of all the capsules contain benzene, whereas at 22 volume % benzene, about one-half of the capsules are thus occupied. These results are consistent with a direct competition between benzene and $CDCl_3$ for the cavity of 5-5. A $^{13}C$ NMR experiment with $^{13}C$-labeled benzene ($^{13}C_6H_6$) conclusively established that the new species is 5-5 with benzene inside its cavity (Fig. 3). Similarly, titration of a *p*-xylene-$d_{10}$ solution of 5-5 with cyclohexane revealed a new upfield (−0.87 ppm) signal in the $^1H$ NMR spectrum for the encapsulated aliphatic guest.

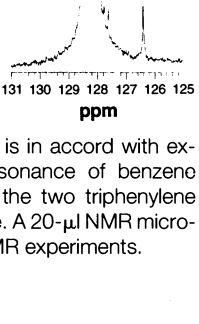

**Fig. 3.** Two $^{13}C$ NMR (125 MHz) spectra. (**Top**) Reference $^{13}C_6H_6$ (5 volume % in $CDCl_3$) and (**bottom**) $^{13}C_6H_6$ (5 volume % in 0.1 M solution of **5-5** in $CDCl_3$). In the reference spectrum, only the $^{13}C$ signal of the cosolvent $^{13}C_6H_6$ and two small signals (presumably arising from coupling with natural abundance of deuterium) are observed. In the presence of the host system, a new signal appears. The 2-ppm upfield shift of the new signal is in accord with expectations for the $^{13}C$ resonance of benzene when positioned between the two triphenylene surfaces of the host capsule. A 20-μl NMR microcell was used for all $^{13}C$ NMR experiments.

The driving force for encapsulation is enthalpic and arises from favorable van der Waals interactions between the convex surface of the guest molecule and the concave surface of the host molecule. However, the loss of entropy (the decreased translational freedom of the confined guest molecule) resists encapsulation. Guests that offer large contact areas and fill the host's cavity (that is, that leave little empty space) without strain are preferred—hence, the affinity for disc-shaped molecules (5). The smaller-than-ideal solvent $CDCl_3$ is displaced by benzene, whereas the larger-than-ideal solvent *p*-xylene, which is poorly accommodated by the capsule, is readily displaced by the more complementary cyclohexane (6). The excellent fit of cyclohexane within 5-5 is shown in the energy-minimized (7) structure of Fig. 4.

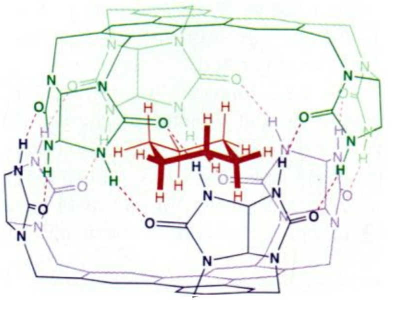

**Fig. 4.** Energy-minimized representation of the dimer **5-5** (the isoamyl ester groups have been omitted for clarity).

The rate at which guest molecules pass into and out of the capsule 5-5 is also unique. Whereas equilibrium distribution between the different host-guest species is rapidly attained in $CDCl_3$-benzene solution, the behavior is entirely different in *p*-xylene-cyclohexane solution. Here, the rate of exchange is slow on the NMR and macroscopic scales: The encapsulation of cyclohexane in *p*-xylene takes hours to reach equilibrium. This was established by observation of the guest-guest exchange process: An equilibrated mixture of 5-5 and excess cyclohexane-$h_{12}$ in *p*-xylene (all capsules contain $C_6H_{12}$) was diluted with equal amounts of cyclohexane-$d_{12}$. The decrease of encapsulated cyclohexane-$h_{12}$ was monitored (Fig. 5), showing that the half-life of the exchange process lies in the range of 2.5 hours. The slow rate indicates that a sizable fraction of the 12 hydrogen bonds of 5-5 must be broken to permit the exit and entry of guest molecules.

As a large part of the interior surface of 5-5 consists of π-bonded atoms, weakly acidic guests may be especially welcome within. The cavity may even be roomy enough to act as a reaction chamber for complementary reaction partners or transition states. The Diels-Alder cycloaddition of ethylene with butadiene or the Claisen rearrangement readily come to mind in this context.

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# Design of a Random Quantum Spin Chain Paramagnet: $Sr_3CuPt_{0.5}Ir_{0.5}O_6$

Tu N. Nguyen, Patrick A. Lee, Hans-Conrad zur Loye*

**A new class of magnetic behavior, random quantum spin chain paramagnetism, has been observed in the one-dimensional compound $Sr_3CuPt_{1-x}Ir_xO_6$. A random quantum spin chain system has $S = \frac{1}{2}$ spins coupled by Heisenberg exchange interactions that are randomly ferromagnetic or antiferromagnetic between neighbors along the chain. This condition was fulfilled by members of the solid solution $Sr_3CuPt_{1-x}Ir_xO_6$ ($x = 0, 0.25, 0.50, 0.75$, and 1), whose end-members, $Sr_3CuPtO_6$ and $Sr_3CuIrO_6$, are antiferromagnetic and ferromagnetic, respectively. Magnetic susceptibility data for the solid solution $Sr_3CuPt_{1-x}Ir_xO_6$ ($x = 0, 0.25, 0.50, 0.75$, and 1) were collected and were found to be in excellent agreement with a theoretical model.**

Low-dimensional materials, both one- and two-dimensional (1D and 2D), have long been of interest to chemists and physicists because of their distinctive electronic and magnetic properties. The strong directionality of low-dimensional structures can produce highly anisotropic physical properties because interactions between electrons, such as magnetic coupling, can depend strongly on the crystallographic directions along which they occur. A wide variety of interesting phenomena have been observed in low-dimensional solids. Some examples are the appearance of the Haldane gap in Heisenberg chains with integer spins (*1*), the observation of the spin–Peierl's transition in linear $Cu^{2+}$ chains in the inorganic compound $CuGeO_3$ (*2*) and in the organic bis-(dithiolene)-copper-tetrathiafulvalene complex (*3*), the existence of 1D antiferromagnetic ordering in tetramethyl ammonium manganese chloride (TMMC) (*4*) and in dichloro-bis(pyridine) copper(II) (CPC) (*4*), and the observation of 1D random antiferromagnetic exchange in the $S = \frac{1}{2}$ salt quinolinium tetrathiafulvalene (*5*).

Random 2D and 3D spin systems have been studied extensively. At low temperatures, they generally form spin glasses, in which the spins freeze into an infinite variety of ground states because of the frustration generated by the random exchange. In a 1D spin chain, however, frustration does not occur. The ground state is unique: Each spin can point in a direction such that the exchange energy with both its neighbors, whatever its sign, is minimized. This picture describes correctly the ground state of the random classical spin chain, and its entropy at finite temperatures is the same as that of a ferromagnetic chain, which has been solved exactly (*6*). However, when the quantum mechanical nature of the spin is taken into account, and $S = \frac{1}{2}$ is the case where quantum effects are most important, the nature of the ground state and its low-lying excitations is not at all obvious. The random $S = \frac{1}{2}$ chain with purely antiferromagnetic but random exchange has been studied, both experimentally (*5*) and theoretically (*7*, *8*). We have found, however, that the existence of exchange interactions of both signs changes the nature of the states qualitatively. A recent renormalization group analysis (*9*) shows that the case with both signs of exchange belongs to a new universality class, so that the low-temperature behavior is expected to be quite different. Here, we report on a new class of 1D compounds, random quantum spin chains, that consist of $S = \frac{1}{2}$ spins coupled by Heisenberg exchange interactions that are randomly ferromagnetic or antiferromagnetic.

We synthesized and characterized a 1D system that exhibits random quantum spin chain paramagnetism, a magnetic phenomenon that can occur in 1D chains that exhibit random ferromagnetic and antiferromagnetic coupling within the chains. The theory developed by Furusaki *et al.* (*10*), which explains the magnetic data of such 1D materials, prompted us to attempt this synthesis. We had been investigating a series of 1D oxides, $Sr_3MM'O_6$ (Figs. 1 and

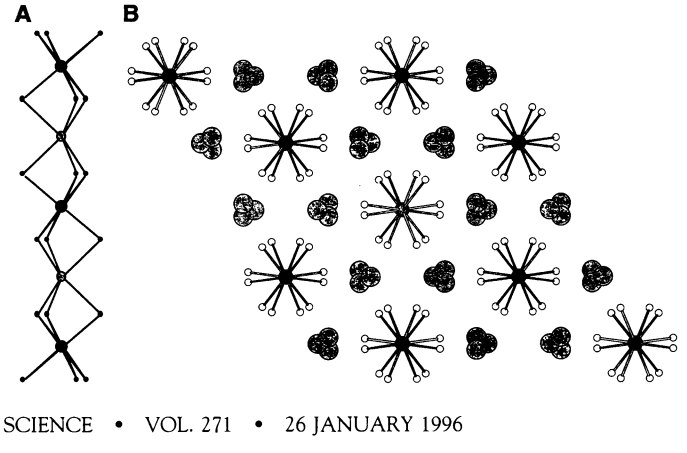

**Fig. 1.** Structure of $Sr_3NiPtO_6$. (**A**) One chain showing alternating octahedra and trigonal prisms; (**B**) structure viewed down the *c* axis. Face-sharing $MO_6$ trigonal prisms alternate with $M'O_6$ octahedra (M = Co, Ni, Zn; M′ = Pt, Ir). These chains are separated by the Sr cations, which maintain charge balance.

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