



50 Years Ago

In the course of two recent geophysical traverses across the Gulf of Guinea, H.M.S. *Hecla* has discovered a number of marked elevations of the ocean bed approximately on a line between St. Helena and the islands of the Bight of Biafra ... The continuous graphical traces made by the precision depth recorder during the traverses indicate that these are rugged topographical features, trending north-east and south-west ... Measured from the abyssal depths from which they rise (2,600 fathoms in the north-west to 3,100 fathoms in the south-east) these features have an elevation exceeding that of the Alps ... The seamants are near and may form part of the submerged feature, shown on certain American bathymetric charts as "The Guinea Ridge".

From *Nature* 24 December 1966

100 Years Ago

Soon after the outbreak of the war, my father, Lord Roberts, asked the public to lend their glasses for the use of the Army. After two years I think your readers may be glad to have some particulars of the result of his request ... Upwards of 26,000 glasses have been received ... The instruments sent comprise every type, and have been classified and issued according to the needs of different units. Particularly useful have been the fine prismatic glasses sent, which have been allocated to artillery and machine-gun units, according to their power; large mounted telescopes for batteries, deer-stalking telescopes for gunners and snipers, and good old-fashioned non-prismatic racing glasses for detection of the nationality of aircraft, locating snipers signalling by disc, collecting wounded, and musketry instruction.

From *Nature* 21 December 1916

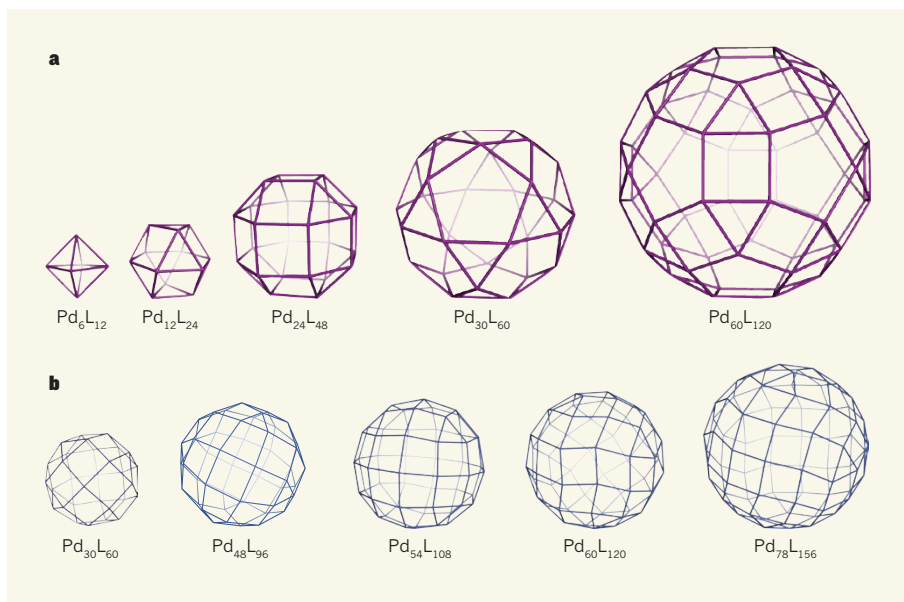


Figure 1 | Self-assembling molecular polyhedra. **a**, Palladium(II) ions (Pd^{2+}) and bipyridyl ligands (L) were predicted⁵ to self-assemble into five possible polyhedra that have the general formula Pd_nL_{2n} , where n can be 6, 12, 24, 30 or 60. The first four of these have been prepared^{6–9} in the past two decades. **b**, While trying to prepare the final member of the series shown in **a**, Fujita *et al.*¹ isolated a structure of formula $\text{Pd}_{30}\text{L}_{60}$, which had an unprecedented topology. They identified this as part of a new infinite series of polyhedra (only five members are shown), and then isolated the next member of this series, $\text{Pd}_{48}\text{L}_{96}$. This achievement opens up research to identify other assemblies of increasing size and complexity.

assemblies; and the preferential formation of ‘isotropic’ structures that have indistinguishable subcomponents to minimize surface energy and distribute local strain equally throughout the assembly. It therefore follows that the most favourable structures are highly symmetrical objects in the shape of Platonic solids (regular convex polyhedra such as cubes or octahedra) or Archimedean solids (semiregular polyhedra composed of different regular polygons that converge at identical vertices).

Additional design constraints also apply, such as the need for palladium ions to bind to ligands in a square-planar geometry — which implies the convergence of exactly four edges at each vertex. Taken together, the constraints on the self-assembly of palladium ions with bifunctional ligands reduce the number of potential target structures to five cages of formula Pd_nL_{2n} , in which n can be 6, 12, 24, 30 or 60, and L is the ligand⁵ (Fig. 1a).

Over the past two decades, Makoto Fujita’s research group has pioneered self-assembly by synthesizing representatives of the first four members of the series: the Pd_6L_{12} octahedron⁶; the $\text{Pd}_{12}\text{L}_{24}$ cuboctahedron⁷; the $\text{Pd}_{24}\text{L}_{48}$ rhombicuboctahedron⁸; and the $\text{Pd}_{30}\text{L}_{60}$ icosidodecahedron⁹. The type of structure that forms depends on the ligand design. For example, subtle changes in the angle formed between the two pyridyl units in a bipyridyl ligand can induce $\text{Pd}_{24}\text{L}_{48}$ stoichiometry to form, rather than $\text{Pd}_{12}\text{L}_{24}$ (ref. 8).

In the present work, Fujita *et al.* targeted the elusive $\text{Pd}_{60}\text{L}_{120}$ rhombicosidodecahedron, the

last representative of the series. However, the authors serendipitously discovered the formation of a $\text{Pd}_{30}\text{L}_{60}$ cage whose single-crystal X-ray structure clearly differed from the previously reported one⁹, and the topology of which did not correspond to any of the Platonic and Archimedean solids. The authors therefore postulated the existence of a new series of polyhedra, which had been reported as theoretical possibilities by mathematicians¹⁰ but never observed in any natural or artificial assemblies: closed-shell frameworks in which eight equally distributed triangles are incorporated into a system of squares (Fig. 1b). These structures are reminiscent of Goldberg polyhedra, which consist of 12 pentagons connected by hexagons, and which are ubiquitous in natural and biological systems — such as fullerene structures and virus capsids.

Impressively, the authors also predicted that the next homologue of the series, $\text{Pd}_{48}\text{L}_{96}$, would be more stable than the isolated compound, and were able to manually separate individual crystals of this larger assembly from the products of their reaction. This cage is by far the most complex molecular structure of precise atomic composition to have been synthesized until now, and is constructed from 144 components through 192 individual metal–ligand interactions.

What is the largest cage structure that could be self-assembled? The extended Goldberg series of polyhedra provides an indefinite number of ever-greater structures, so in principle there is no intrinsic limit to size. However, it will be increasingly difficult to