A synthetic molecular pentafoil knot

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Knots are found in DNA and proteins and even in the molecules that make up natural and man-made polymers, where they can play an important role in the substance's properties. For example, up to 85% of the elasticity of natural rubber is thought to be due to knot-like entanglements in the rubber molecules chains. However, deliberately tying molecules into knots so that these effects can be studied is extremely difficult. Up to now only the simplest types of knot, the trefoil knot with three crossing points and the topologically-trivial unknot with no (zero) crossing points, have succumbed to chemical synthesis using non-DNA building blocks. Here we describe the first small-molecule pentafoil knot, which is also known as a cinquefoil knot or a Solomon's seal knot — a knot with five crossing points that looks like a five-pointed star. The structure of the knot was determined using data collected on I19 through the Engineering and Physical Sciences Research Council (EPSRC) National Crystallography Service. Making knotted structures from simple chemical building blocks should make it easier to understand why entanglements and knots have such important effects on material properties and may also help scientists to make new materials with improved properties based on knotted molecular architectures.

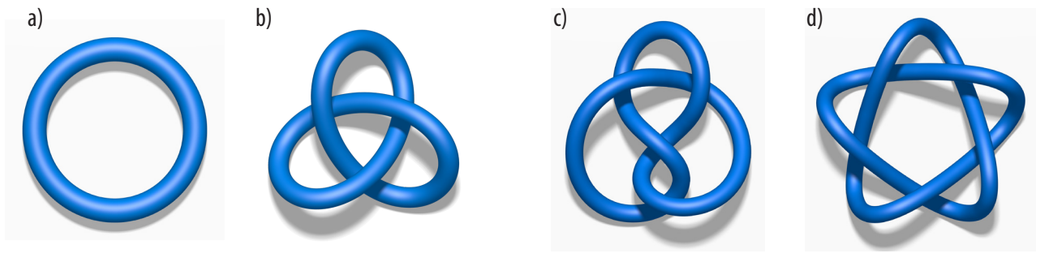

Figure 1: The topologies of the four simplest prime knots: (a) unknot (zero crossing points); (b) trefoil knot (three crossing points); (c) figure-of-eight knot (four crossing points); (d) pentafoil knot (five crossing points).

Knots are important structural features in DNA. They are found in some proteins and play a significant role in the physical properties of both natural and synthetic polymers.[1] Although billions of prime knots are known to mathematics[2], to date the only ones to have succumbed to chemical synthesis using building blocks other than DNA, are the topologically-trivial unknot, i.e. a simple closed loop without any crossing points (Fig. 1a) and the next simplest knot, featuring three crossing points, the trefoil knot[1,2] (Fig. 1b). A pentafoil knot (Fig. 1d) or cinquefoil knot (the 5_1 knot in Alexander-Briggs notation[2]) — is a torus knot[2] with five crossing points, is inherently chiral, and is the fourth prime knot (following the unknot, trefoil knot and figure-of-eight knot (Fig. 1c)) in terms of number of crossing points and complexity[2].

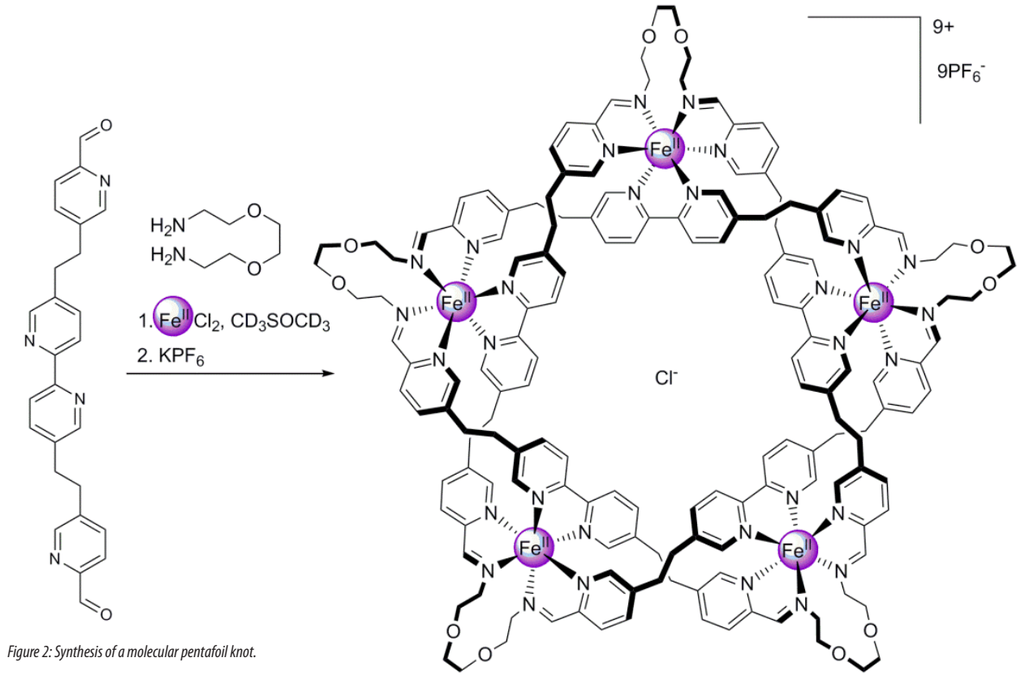

Figure 2: Synthesis of a molecular pentafoil knot.

The synthesis of a molecular pentafoil knot was achieved in a one-pot, 16-component self-assembly reaction by combining the use of metal helicates to create crossover points[3], anion template assembly to form a cyclic array of the correct size[4], and the joining of the metal complexes by reversible imine bond formation,[5] aided by the *gauche* effect to make the continuous 160-atom-long covalent backbone of the molecular knot (Fig. 2).

Single crystals of the molecular pentafoil knot were obtained by slow diffusion of diethyl ether vapour into a solution of the knot in acetonitrile:toluene (3:2) and the solid-state structure determined by X-ray crystallography on station I19. The crystal structure (Fig. 3) confirmed the topology and symmetry of the molecular pentafoil knot. The single organic ligand weaves a continuous path about the five co-planar iron centres, the loop passing over and under itself each time it wraps around a metal ion. At the centre of the structure is a chloride anion, held in place by ten CH···Cl^- hydrogen bonds.

The pentafoil knot has symbolic significance in many ancient and modern cultures and religions (as does its two-dimensional projection, the pentagram) and features as the central emblem on the present day flags of both Morocco and Ethiopia. The practical significance of its preparation in molecular form includes the lessons learned from the multitude of different structural design features used in its assembly and the potential for the synthesis of higher order structures with precisely defined knotted architectures that may enable the role of entanglements in molecular materials to be elucidated and exploited.

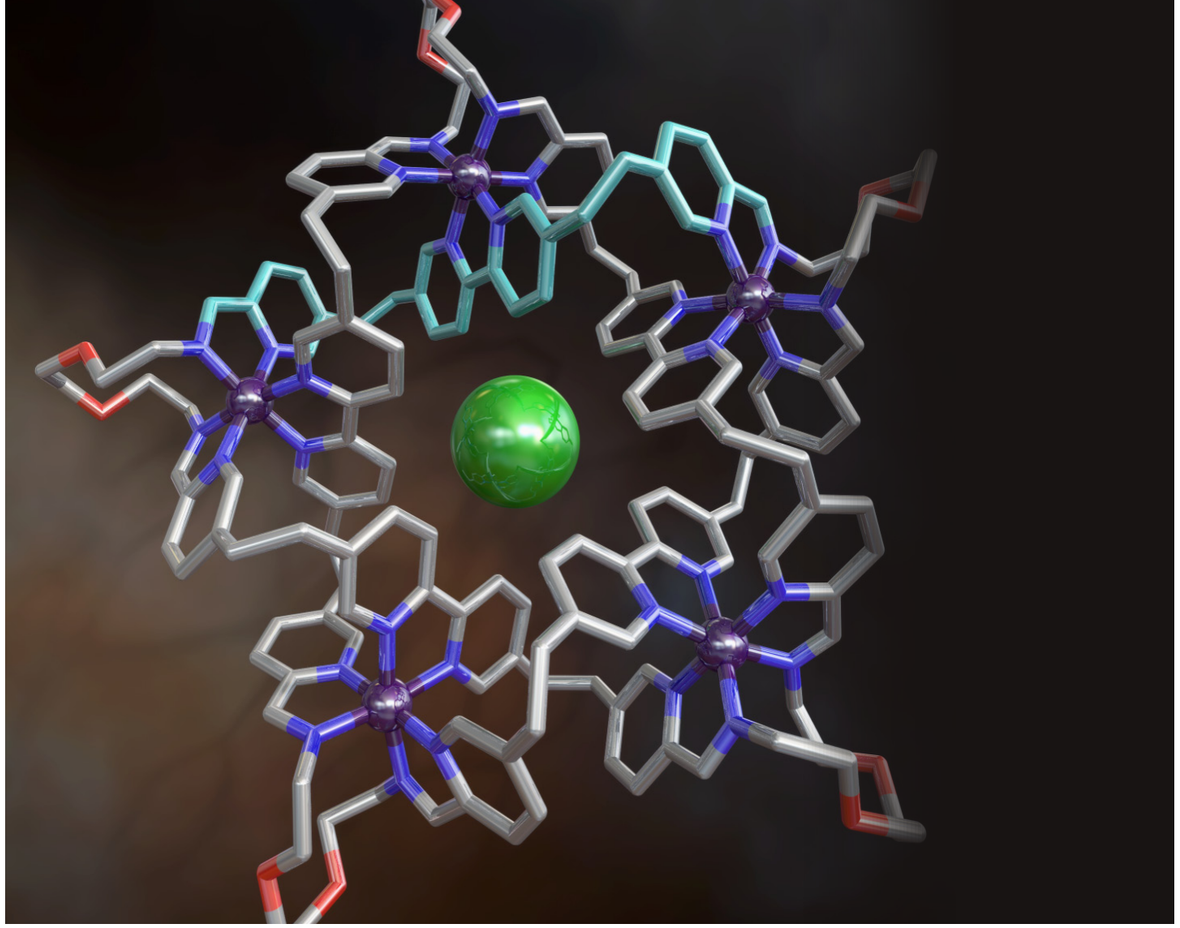

Figure 3: X-Ray crystal structure of a molecular pentafoil knot. (Image credit: Robert W. McGregor (www.mcgregorfineart.com).)

References

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