Researchers create most tangled interlocked molecule ever

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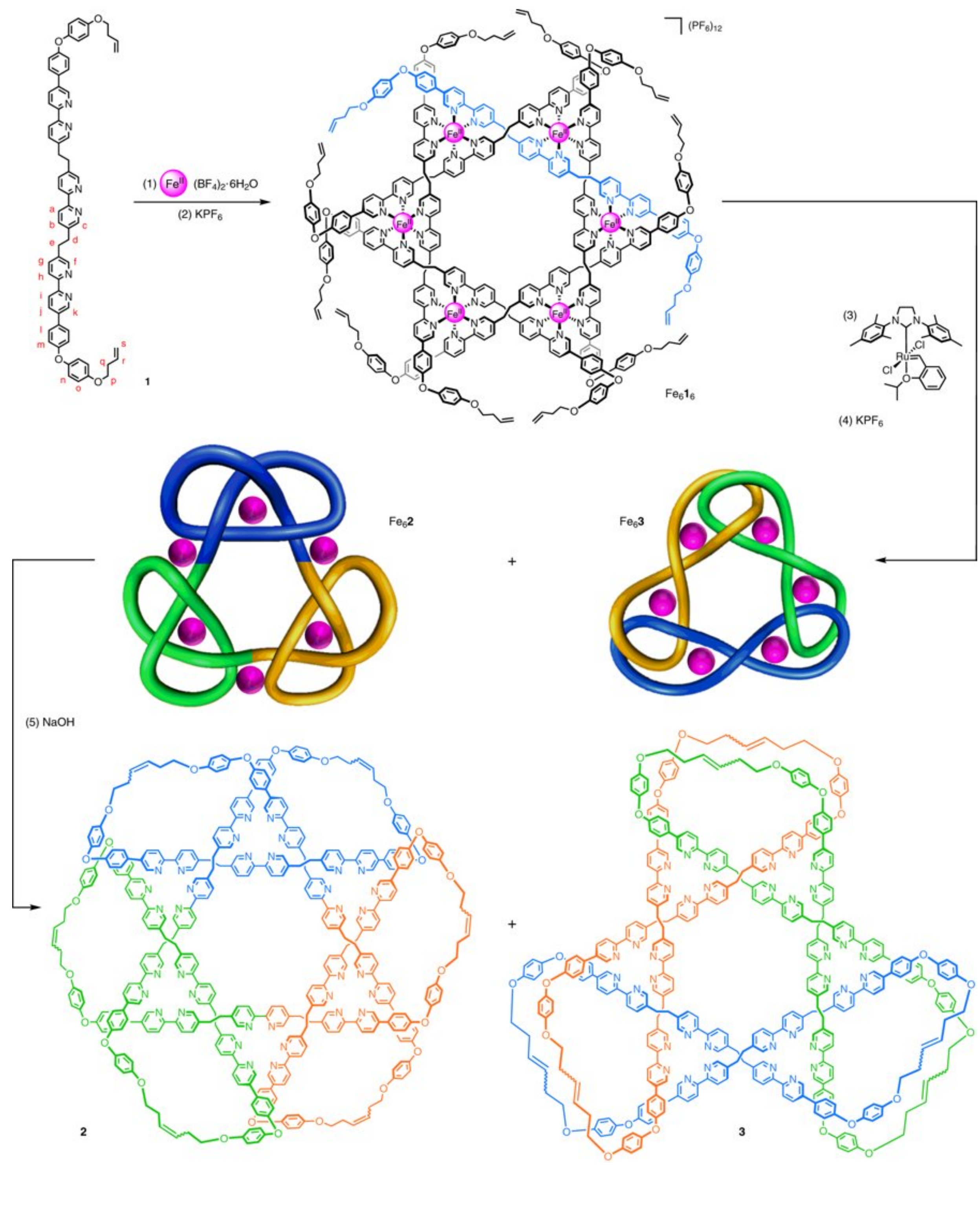

The 12 component (6 × ligand 1; 6 × Fe^{2+}) assembly of the intermediate hexameric circular helicate $[Fe_6 1_6](PF_6)_{12}$ and the synthesis of the +31#+31#+31 composite knot 2 and 9^3_7 link 3. Credit: *Nature Chemistry* (2018). DOI: 10.1038/s41557-018-0124-6

A team of researchers at the University of Manchester has created the most tangled interlocked molecule ever. In their paper published in the journal *Nature Chemistry*, the group describes creating the knot and their hope that such knots will one day become useful. Edward Fenlon with Franklin & Marshall College offers a News and Views piece on the work done by the team in the same journal issue.

Tying molecules into knots is a relatively new field—scientists have only been doing it for a decade. It is also unique because thus far there are very few if any practical applications for most such knots. Still, some chemists find the work intriguing, so they continue to create new and ever more complicated knots. In this new effort, the team at UM has built on prior work that led to the creation of molecules shaped like the Star of David and one that was deemed by Guinness as the world's tightest—by creating one in the shape of a three-trefoil tangle.

While the name might sound complicated, the three-trefoil tangle is actually quite simple—creating one with a shoelace, for example, can be done by a child. But using a single 324 atom molecular strand molecule to do it takes some work. The group accomplished this feat by starting with six strands, each with an alkene group at its tips—and groups of three bipyridyls in the middle. They then manipulated the ligands to wrap around six iron ions to hold them in place. They finished by using a catalyst to connect the alkenes with a metathesis reaction to remove the iron. The result was a knot with nine crossings. As part of their work, the researchers also created a granny knot by connecting three figure-eight knots together.

The researchers acknowledge that neither of their knots has any practical use at this time, but note that historically, new kinds of knots have been created to suit particular demands. Rock climbers, for example, use knots that are very different from sailors. This suggests that now that chemists know that knots can be made, they might find applications that can benefit from them. They also suggest that learning how to tie molecules in knots can help scientists understand how natural ones occur, such as those in viruses.

More information: Liang Zhang et al. Stereoselective synthesis of a composite knot with nine crossings, *Nature Chemistry* (2018). DOI: 10.1038/s41557-018-0124-6

Abstract

The simultaneous synthesis of a molecular nine-crossing composite knot that contains three trefoil tangles of the same handedness and a 937973 link (a type of cyclic [3]catenane topologically constrained to always have at least three twists within the links) is reported. Both compounds contain high degrees of topological writhe (w = 9), a structural feature of supercoiled DNA. The entwined products are generated from the cyclization of a hexameric Fe(II) circular helicate by ring-closing olefin metathesis, with the mixture of topological isomers formed as a result of different ligand connectivity patterns. The metal-coordinated composite knot was isolated by crystallization, the topology unambiguously proven by tandem mass spectrometry, with X-ray crystallography confirming that the 324-atom loop crosses itself nine times with matching handedness (all Δ or all Λ) at every metal centre within each molecule. Controlling the connectivity of the ligand end groups on circular metal helicate scaffolds provides an effective synthetic strategy for the stereoselective synthesis of composite knots and other complex molecular topologies.