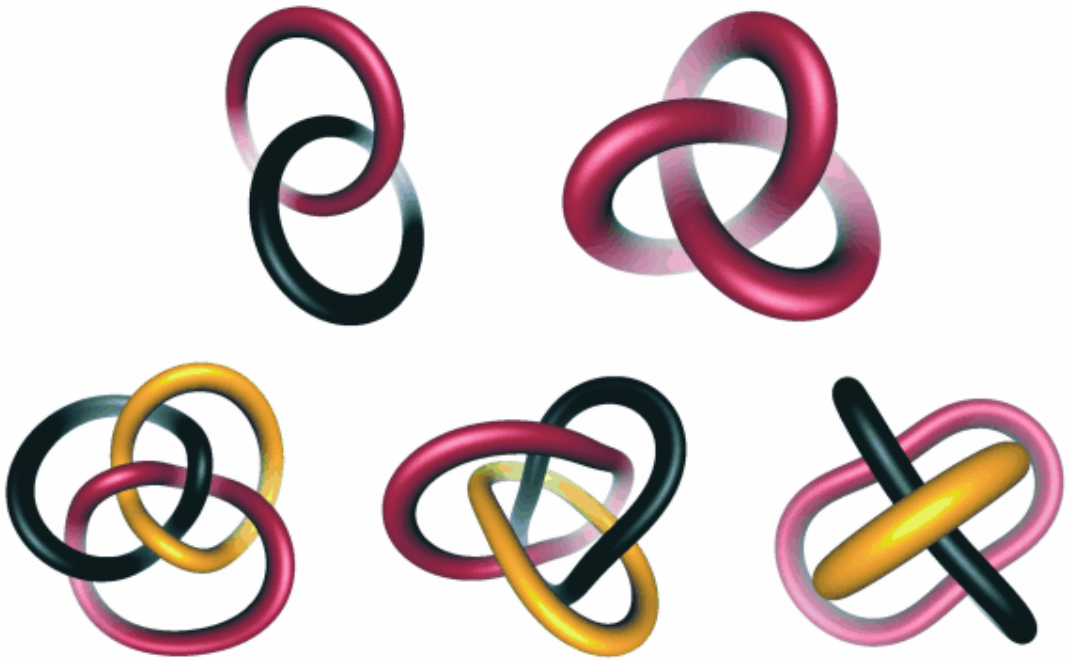
Stereoselective Synthesis of a Topologically Chiral Molecule: The Trefoil Knot

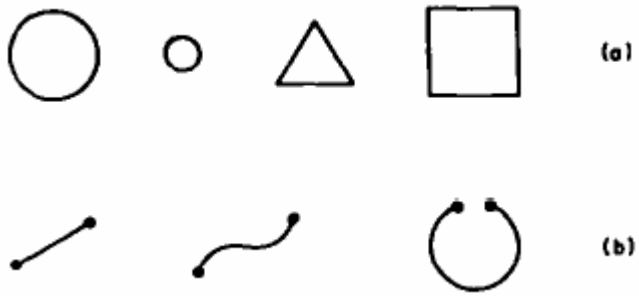


Perret-Aebi, L. E.; von Zelewsky, A.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 4482

Topological Stereochemistry

Topological stereoisomers are those stereoisomers owing their distinct character solely to bond connectivity, requiring no Euclidean molecular rigidity at all to remain chemically different.[1]

Topologically equivalent

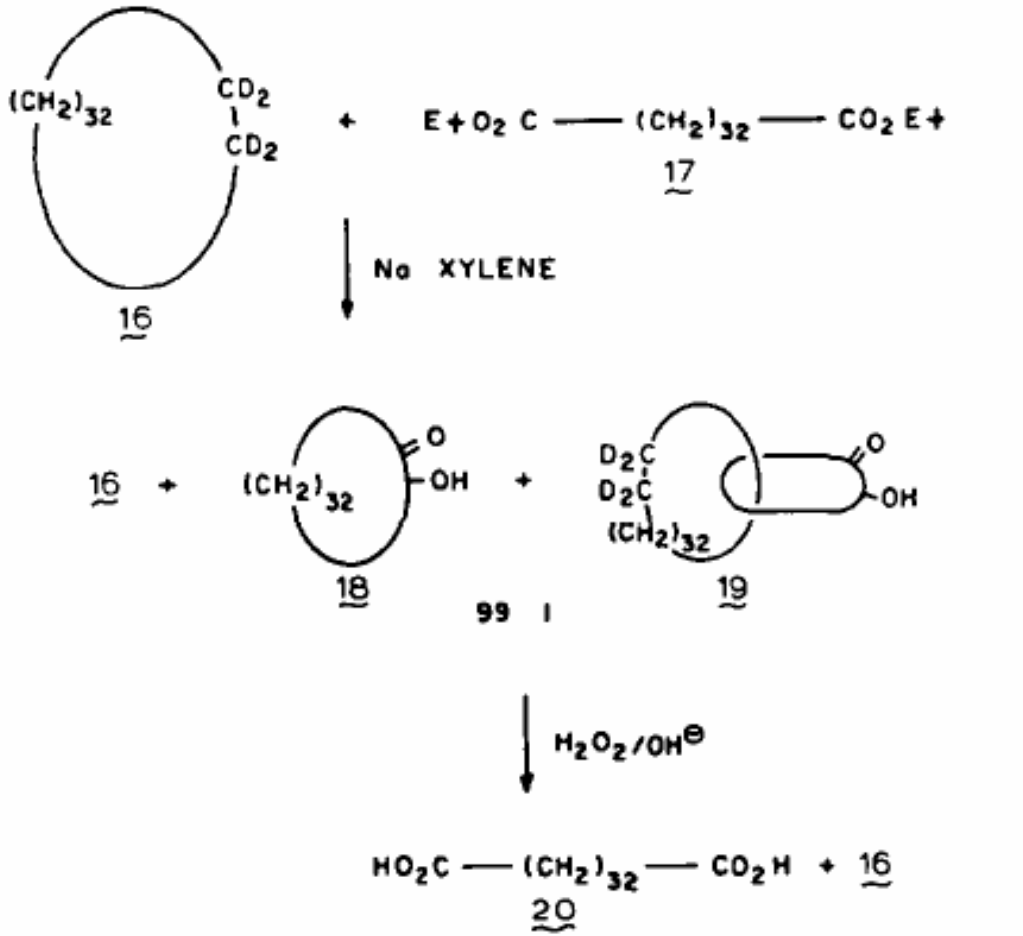


Topology involves geometrical properties which remain invariant given continuous deformation in 3-space. The constructions are considered totally flexible, as though made of infinitely stretchable rubber threads. However, lines may not cross and points may not become congruent. [1]

Topological stereoisomers

[1]Walba, D. A. *Tetrahedron* **1985**, *41*, 3161

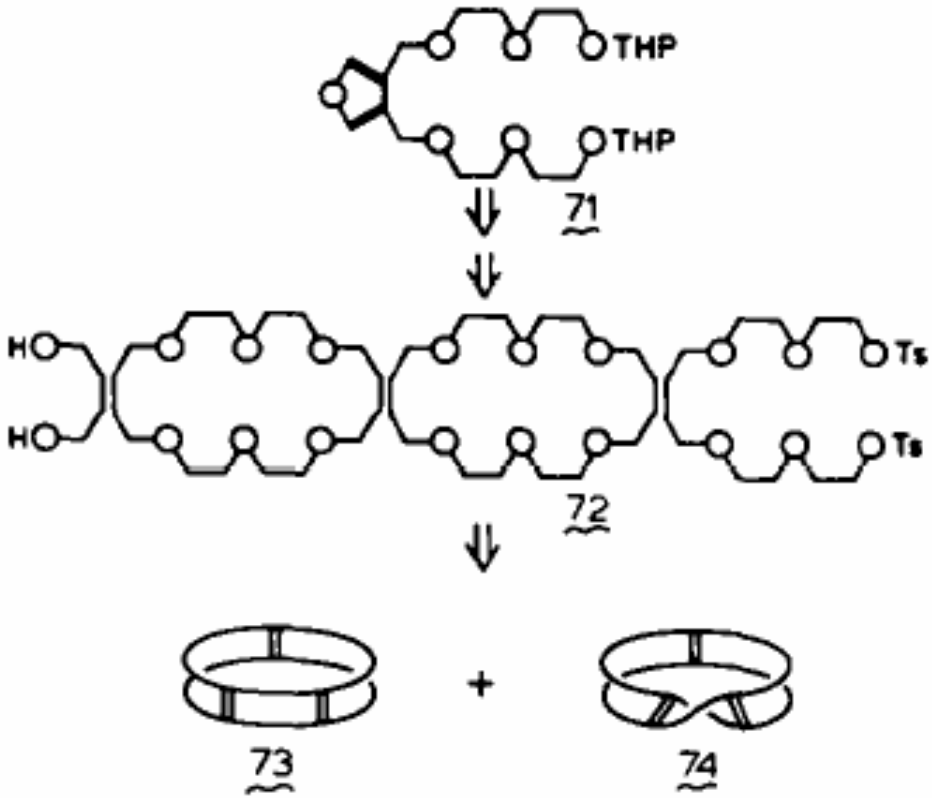
First Synthesis of a Catenane



Scheme 8 The Wasserman catenane synthesis

[1]Wasserman, E. *J. Am. Chem. Soc.* **1960**, *82*, 4433

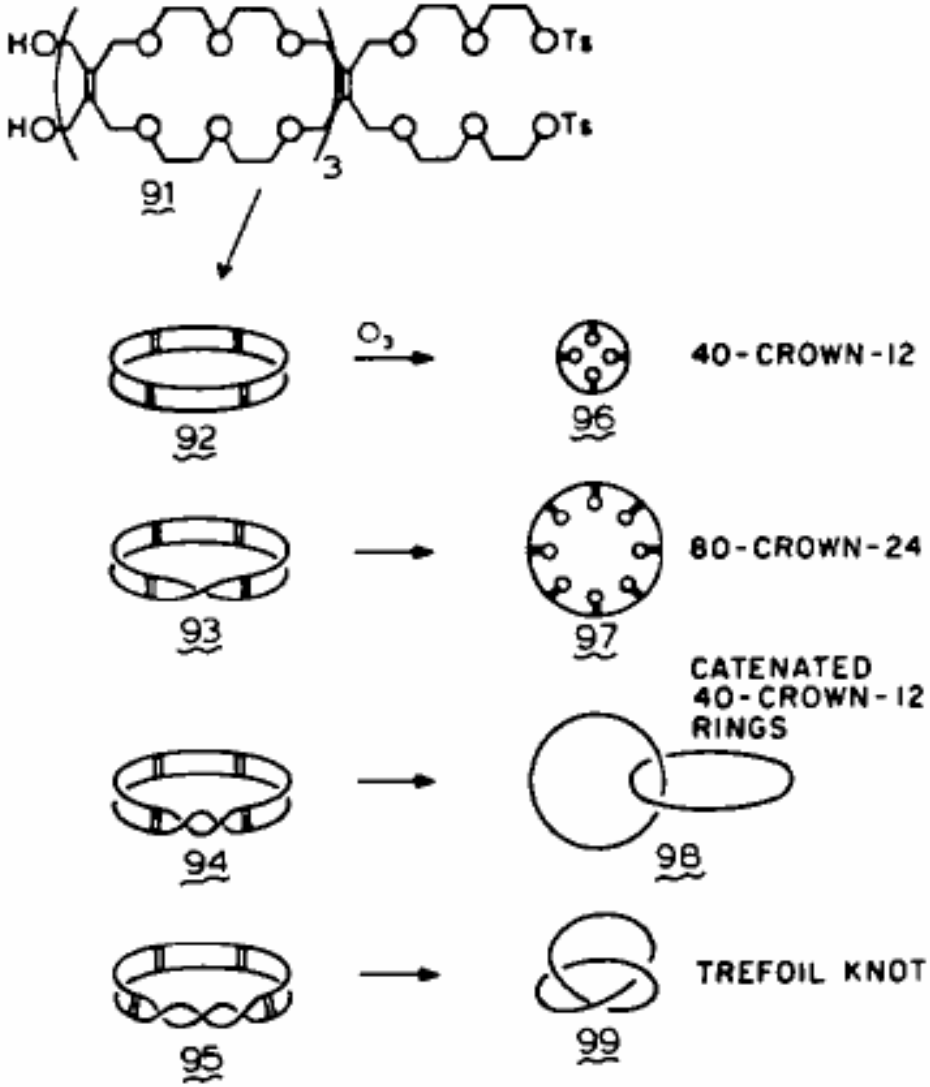
The Synthesis of the First Molecular Möbius Strip



Scheme 23 Synthesis of the first molecular Möbius strip

Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 3219

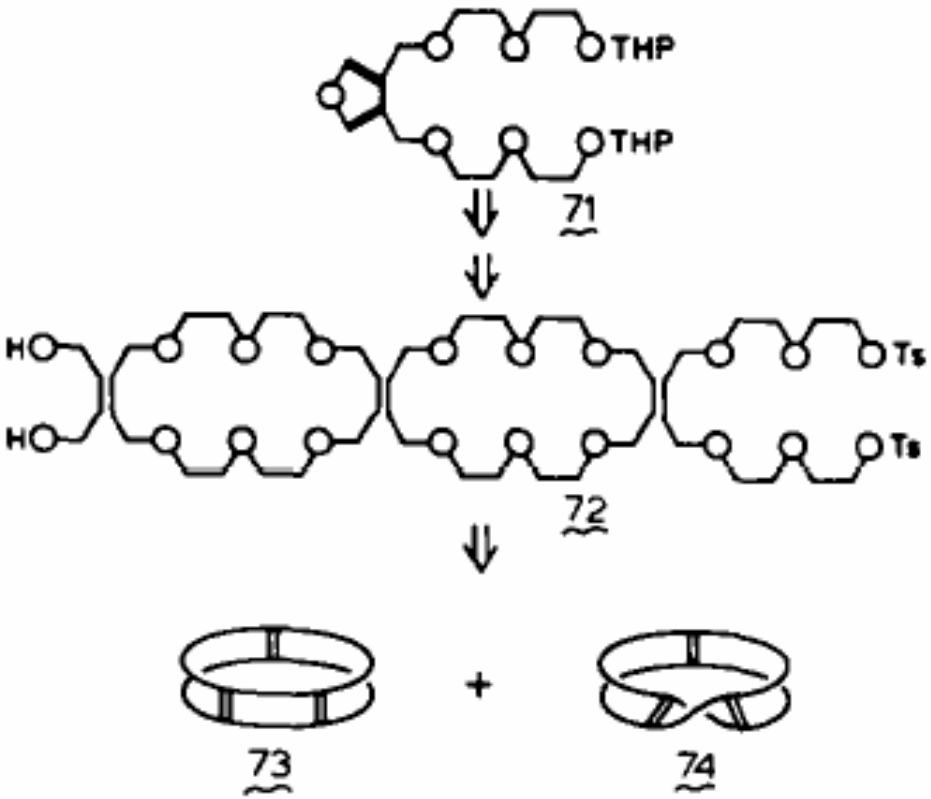
The Möbius Strip Approach to Molecular Knots



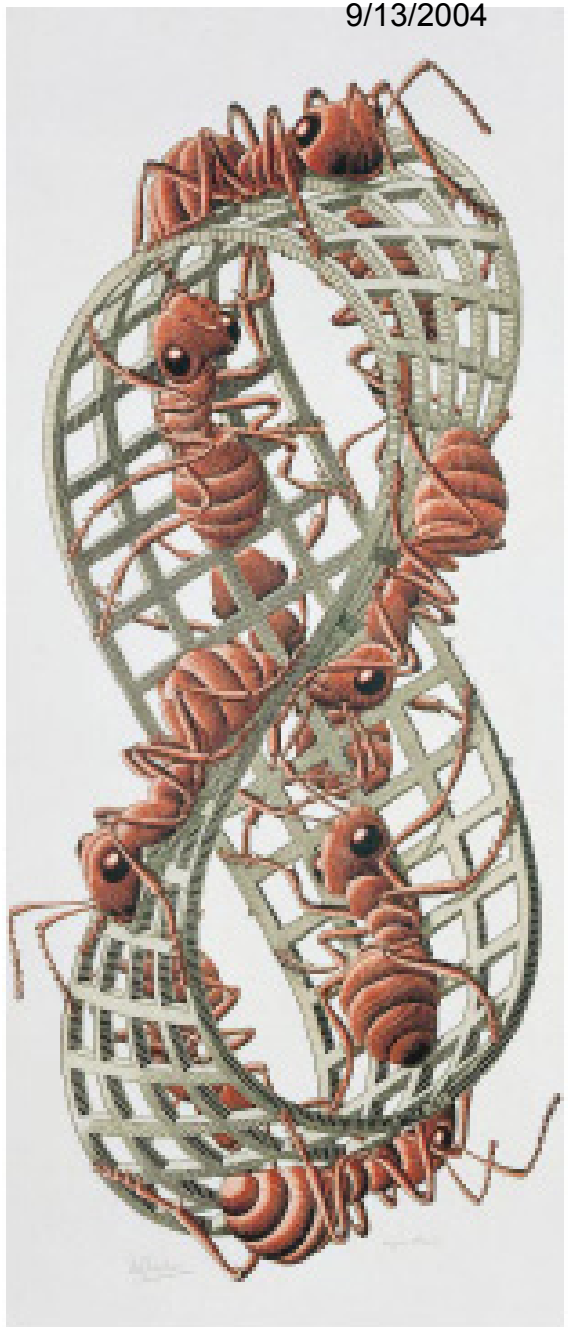
Scheme 31 The THYME approach to synthesis of a trefoil knot

Walba, D. A. *Tetrahedron* **1985**, *41*, 3161

The Synthesis of the First Molecular Möbius Strip



Scheme 23 Synthesis of the first molecular Möbius strip



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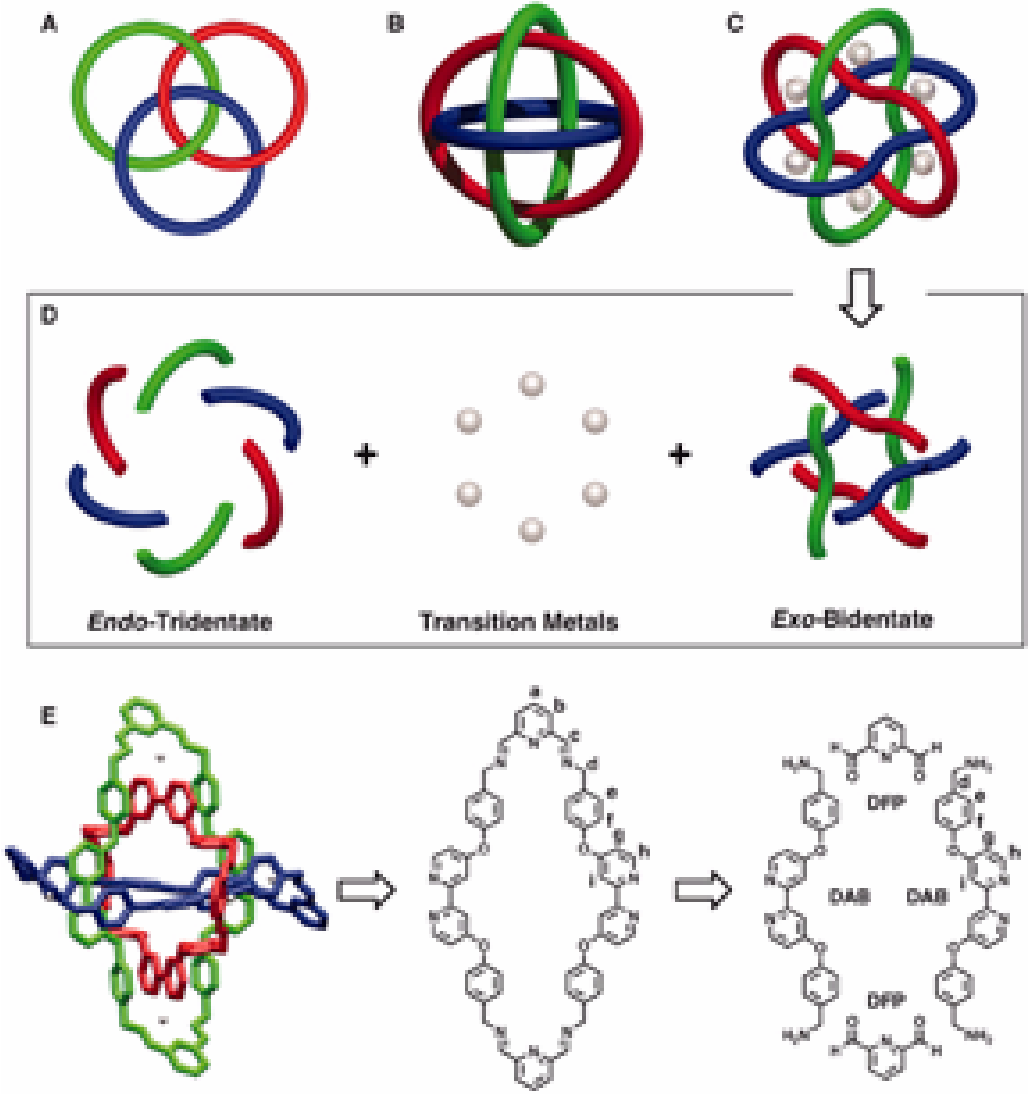
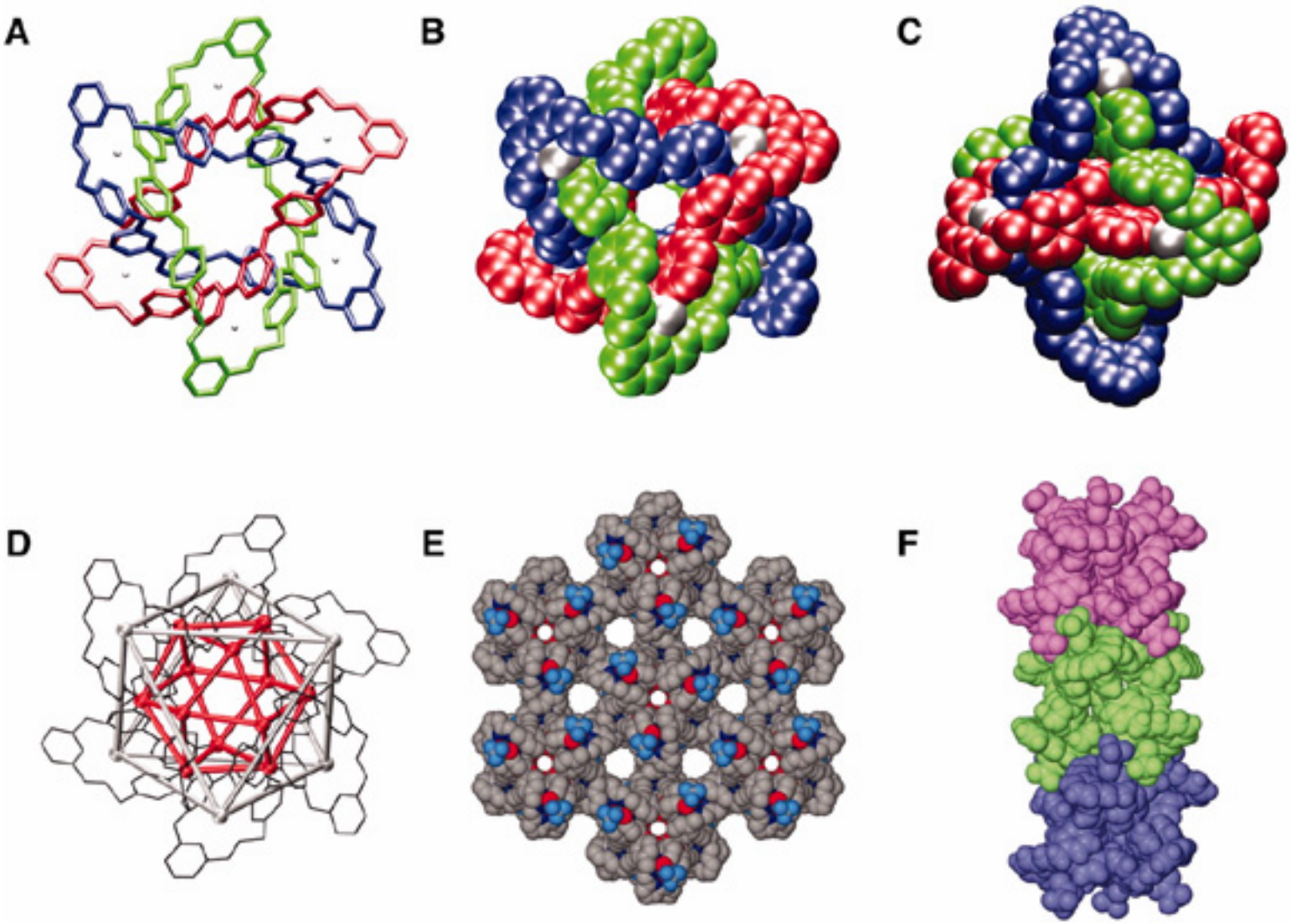
The Synthesis of Molecular Borromean Rings



Chickak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S.-H.; Cave, G. W. V.; Atwood, J. L.; Stoddart, J. F. *Science* **2004**, *304*, 1308

The Synthesis of Molecular Borromean Rings



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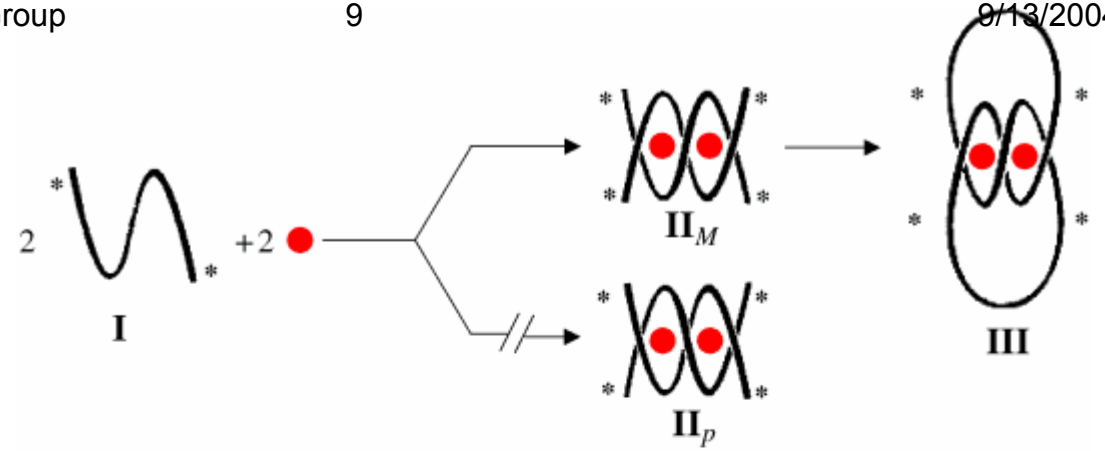
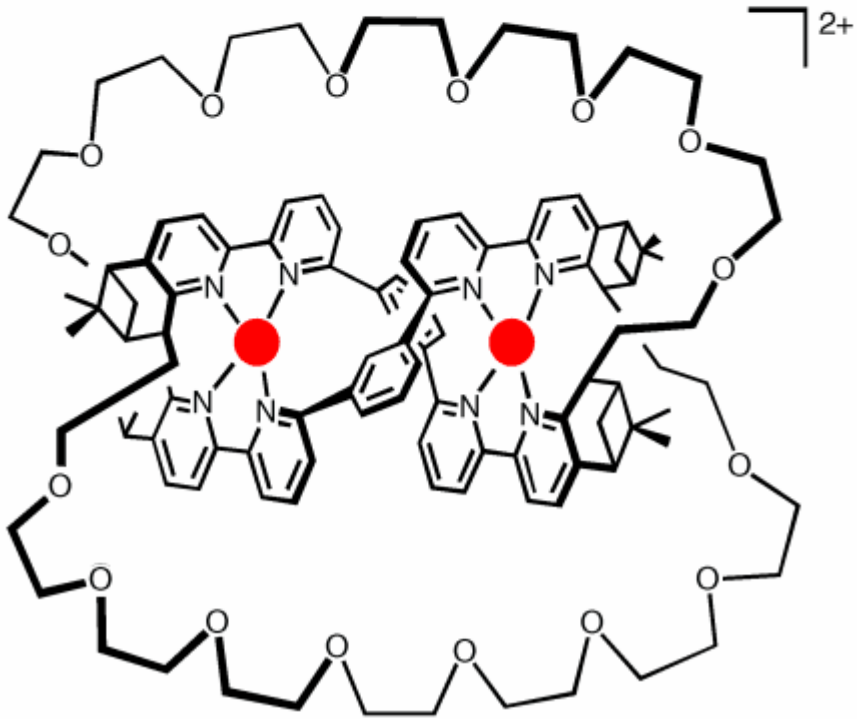
The Synthesis of a Molecular Trefoil Knot



III ≡



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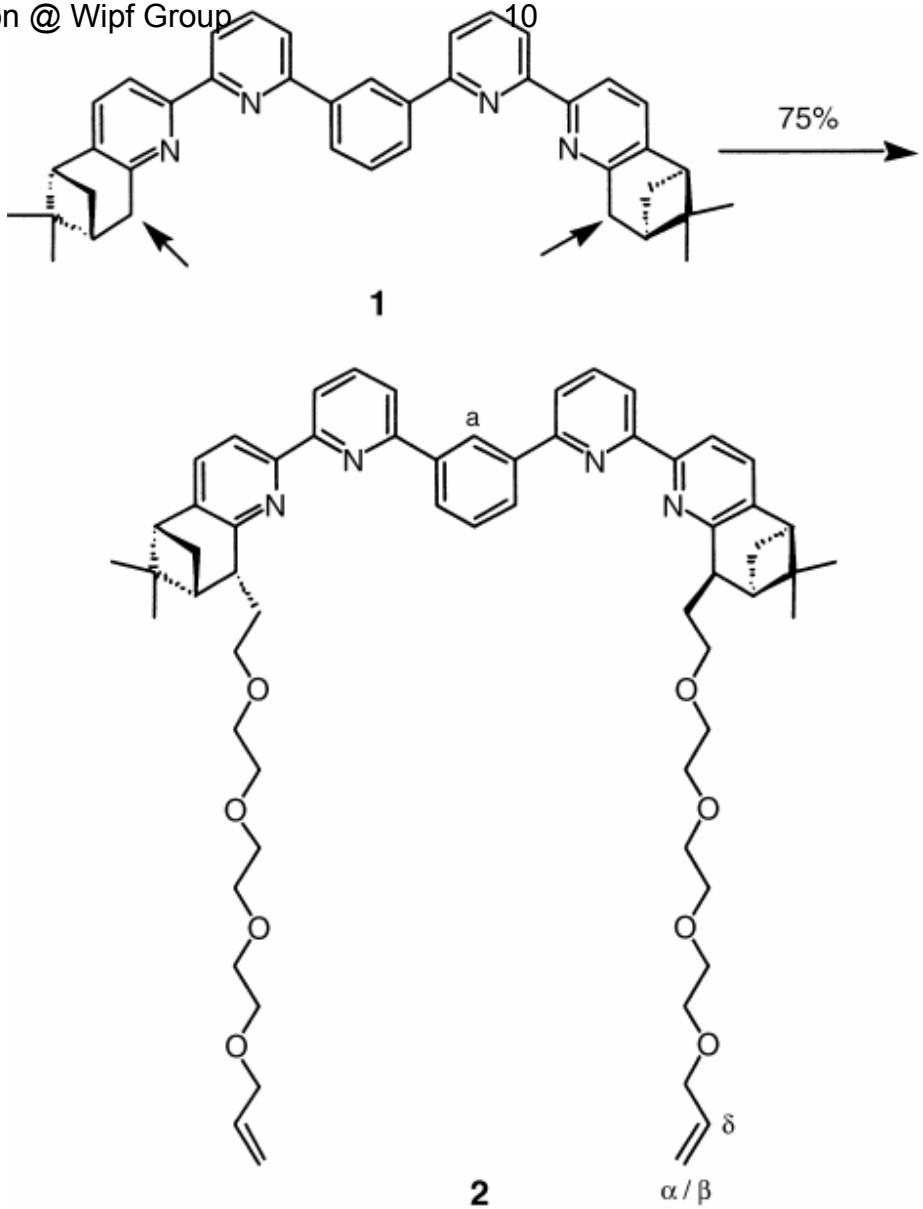

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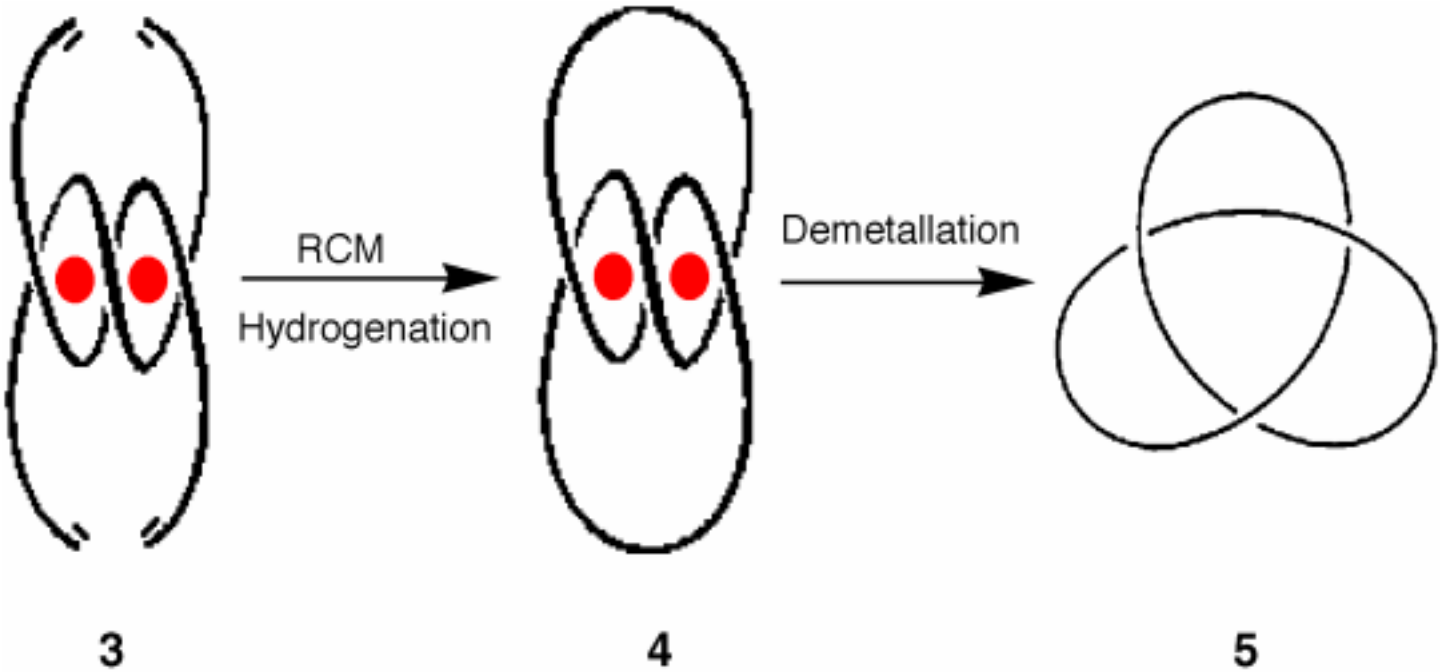

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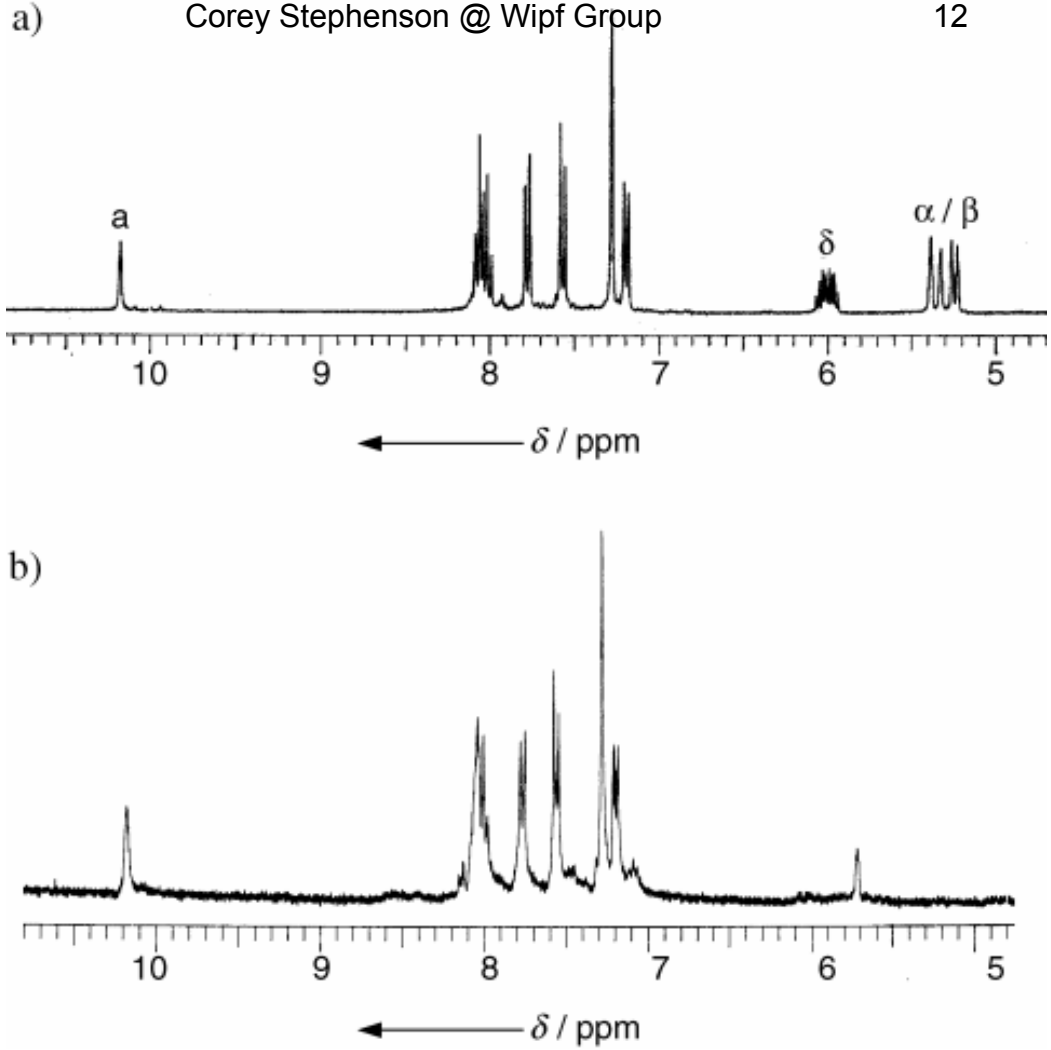
The Synthesis of a Molecular Trefoil Knot



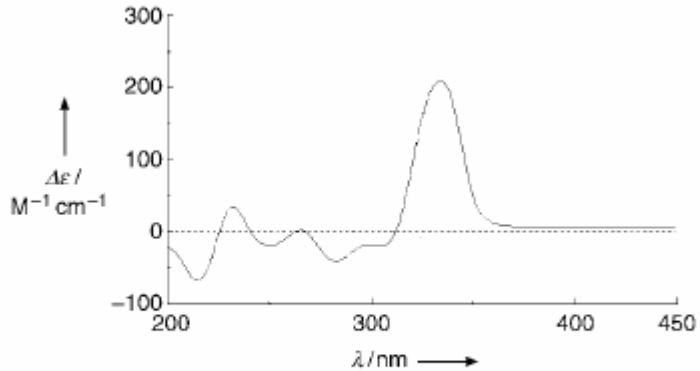


Figure 6. CD spectrum ($\Delta\varepsilon$ = molar circular dichroism) of the left-handed knotted system **4**.

"Unfortunately, we were not able to obtain crystals of either 3 or 4 that were suitable for X-ray crystallographic studies"

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Summary

- A concise synthesis of a molecular trefoil knot has been achieved using an efficient templated ring-closing metathesis reaction
- The structural assignment was supported by MS and ^{1}H NMR studies
- Circular dichroism studies used to confirm the formation of a topologically chiral molecule