

A Star of David catenane

David A. Leigh*, Robin G. Pritchard and Alexander J. Stephens

We describe the synthesis of a [2]catenane that consists of two triply entwined 114-membered rings, a molecular 6_1^2 link. The woven scaffold is a hexameric circular helicate generated by the assembly of six tris(bipyridine) ligands with six iron(II) cations, with the size of the helicate promoted by the use of sulfate counterions. The structure of the ligand extension directs subsequent covalent capture of the catenane by ring-closing olefin metathesis. Confirmation of the Star of David topology (two rings, six crossings) is provided by NMR spectroscopy, mass spectrometry and X-ray crystallography. Extraction of the iron(II) ions with tetrasodium ethylenediaminetetraacetate affords the wholly organic molecular link. The self-assembly of interwoven circular frameworks of controlled size, and their subsequent closure by multiple directed covalent bond-forming reactions, provides a powerful strategy for the synthesis of molecular topologies of ever-increasing complexity.

A hexagram is a six-pointed geometric star consisting of two interwoven triangles that cross each other six times in its three-dimensional representation, a 6_1^2 link in Alexander–Briggs notation¹. It has long been used as a religious, cultural and artistic symbol² and is today the generally recognized symbol of Judaism (the ‘Star of David’ or, in Hebrew, ‘Magen David’ (Shield of David)). Molecular links (catenanes³) have been targets for rational synthesis for more than half-a-century⁴. This is, in part, because of their potential applications (complex links of proteins form bacteriophage capsid ‘chainmail’⁵ and the large amplitude motions of interlocked rings can be exploited in artificial molecular machinery⁶), but also because they are fundamental elements of structure^{7–9} that have historically proved challenging to create in molecular form¹⁰. Five rings have been linked in a linear array¹¹, and examples of Borromean rings^{12,13} (interlocked assemblies within which no two rings are linked), doubly entwined catenanes (Solomon links^{14–22}), [3]catenanes²³ and interpenetrated cages^{24–28} have been reported. To date, however, triply entwined molecular links remain elusive.

The Sauvage group reported²⁹ attempts to prepare a Star of David catenane by connecting the termini of linear double-stranded pentametal helicates; the two-and-a-half turns of the double helix plus the ring-closing reactions should, in principle, generate the six crossings necessary for the triply entwined topology. However, the approach proved unsuccessful, probably as a result of the considerable distance between the reactive end groups of the linear helicates. Circular helicates offer the possibility of much shorter distances for ring closure, regardless of the number of crossings created, at the expense of an increase in the number of bond-forming reactions required^{21,30–32}. Here we report on the use of a hexameric circular helicate scaffold to assemble a Star of David catenane.

The route to the Star of David catenane is shown in Fig. 1. We were unable to find conditions under which imine ligand strands similar to those used to assemble a molecular pentafoil knot³⁰ formed hexameric circular helicates³¹. Accordingly, ligand **1** is based on the tris(2,2′-bipyridine) motif found by Lehn and co-workers³³ to form hexameric circular helicates with octahedral iron(II) cations, with the ring size selected by the use of sulfate counterions. However, in such circular helicates the adjacent terminal bipyridine residues (which have to be joined to form the Star of David topology) point directly away from each other. Using linearly

extended ligands we were unable to close the resulting circular hexameric helicates, and instead produced oligomers and crosslinked material (see the Supplementary Information). It appeared to be too energetically demanding to restrict the degrees of freedom of flexible chains to form the multiple intrahelicate connections required to make the catenane. Therefore we redesigned the ligand **1** to restrict the conformational space that the olefin end groups could occupy in the open circular hexameric helicate. The phenyl ring attached to each end of the tris(bipyridine) ligand is twisted out of the plane of the adjoining bipyridine group for steric reasons, which greatly restricts the conformational space accessible by the attached alkene chain. The *ortho*-substitution pattern brings the alkenes of adjacent ligand strands into close proximity in a low-energy conformation such that intracircular helicate covalent-bond formation should be favoured.

Results and discussion

On heating **1** with an equimolar amount of FeSO₄ in ethylene glycol at 170 °C for 24 hours, an intense red–purple solution was obtained, indicative of the formation of low-spin iron(II) tris(bipyridine) complexes (Fig. 1, step i). The major product was isolated in 75% yield as the hexafluorophosphate salt by precipitation using aqueous KPF₆, followed by filtration and washing with methanol and dichloromethane (Fig. 1, step ii). Electrospray ionization mass spectrometry (ESI-MS) showed *m/z* peaks that correspond to the sequential loss of PF₆[−] counterions, consistent with the hexameric circular helicate structure [2](PF₆)₁₂. The ¹H NMR spectrum (600 MHz, CD₃CN/CDCl₃ (1:1), 298 K (Fig. 2c)) is highly symmetric, with all six ligands equivalent and each individual strand of **1** possessing two-fold symmetry. The diastereotopic splitting of the pairs of H^a and H^b protons of the ethylene bridges in [2](PF₆)₁₂ is a further indication of a helical structure.

A second, minor, product was isolated from the dichloromethane washings. The ¹H NMR spectrum (Fig. 2b) was consistent with this complex also having a helical structure (for example, diastereotopic CH₂^a and CH₂^b (Fig. 2b)) and ESI-MS indicated it to be the linear triple helicate [3](PF₆)₆ (refs 31,34). The ratio of [2](PF₆)₁₂: [3](PF₆)₆ could be varied from 4:96 to >98:2 by changing the reaction conditions and ligand:iron(II) ratio (see the Supplementary Information), with higher concentrations and close-to-stoichiometric ratios of 1:FeSO₄ favouring the circular hexameric helicate [2](PF₆)₁₂.

School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK. *e-mail: david.leigh@manchester.ac.uk

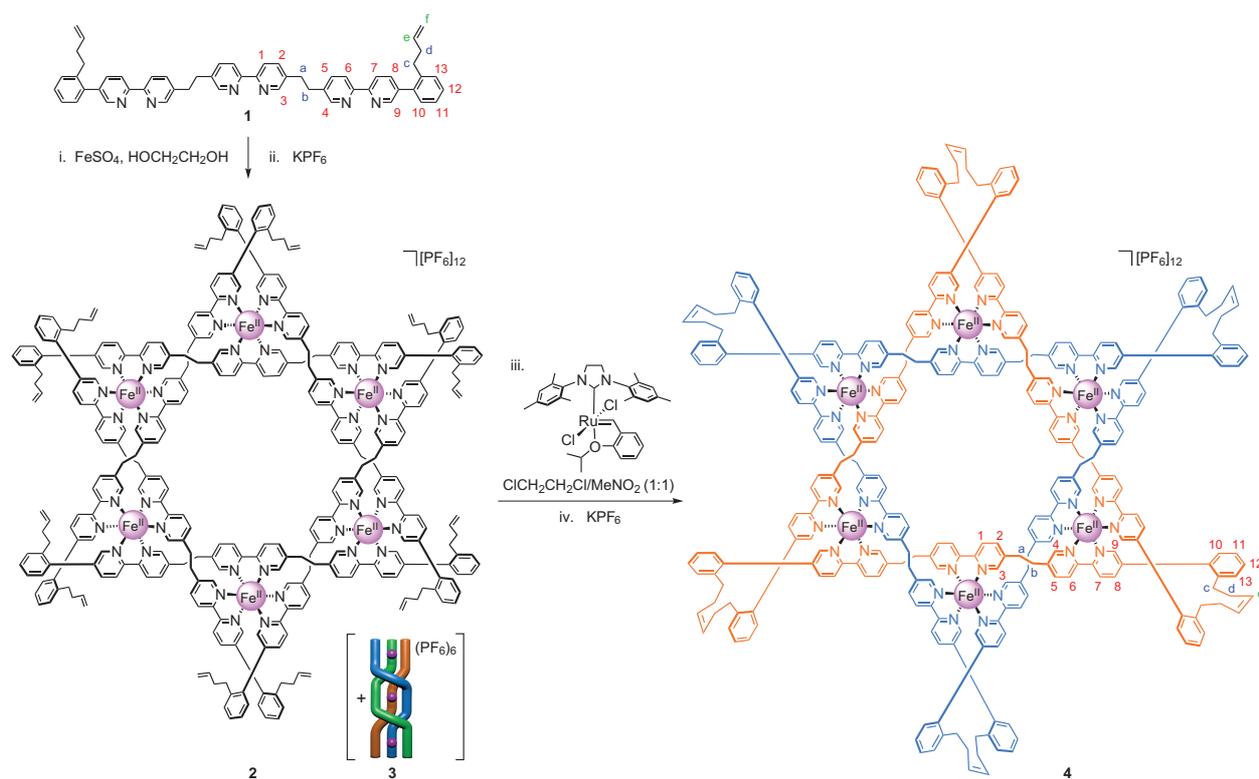


Figure 1 | Assembly of a hexameric circular iron(II) helicate $[2](PF_6)_{12}$ and subsequent ring closure to form a Star of David $[2]$ catenate, $[4](PF_6)_{12}$. Reaction conditions: i, ethylene glycol, 170 °C, 24 hours; ii, excess saturated KPF_6 in methanol; iii, dichloroethane/nitromethane (1:1), 60 °C, 24 hours; iv, excess saturated aqueous KPF_6 . The yields and ratios of circular double helicate $[2](PF_6)_{12}$ and linear triple helicate $[3](PF_6)_6$ vary with concentration and equivalents of $FeSO_4$ (see the Supplementary Information). In a representative procedure (14 mM **1**, 1 equiv. $FeSO_4$), $[2](PF_6)_{12}$ was isolated in 75% yield and $[3](PF_6)_6$ in 9% yield. Yield of $[4](PF_6)_{12}$ from $[2](PF_6)_{12}$, 92%.

To close the covalent framework of the hexameric circular helicate, $[2](PF_6)_{12}$ was subjected to ring-closing metathesis (RCM) using the Hoveyda-Grubbs second-generation catalyst³⁵ (Fig. 1, step iii). After 24 hours, ESI-MS indicated the loss of six ethene molecules from the circular helicate, and the reaction was quenched and washed with aqueous KPF_6 to ensure uniformity of the counter-anions (Fig. 1, step iv). The 1H NMR spectrum of $[4](PF_6)_{12}$ (Fig. 2d) confirms the absence of terminal alkene protons and also shows the doubling of many of the signals because rotamerization about the phenyl-bipyridine bond in the open circular helicate is restricted in the $[2]$ catenate (a catenane-metal complex is termed a ‘catenate’ and the interlocked metal-free ligand is a ‘catenand’³⁶) and the two ends of each tris(bipyridine) unit become locked in different chemical environments.

Single crystals of **4** were grown by solvent diffusion of methanol saturated with $NaBPh_4$ into a solution of $[4](PF_6)_{12}$ in acetonitrile, and the solid-state structure determined by X-ray crystallography using the Diamond synchrotron source (see the Supplementary Information). The crystal structure (Fig. 3) confirms the topology and symmetry of the Star of David catenate, with the two interlocked 114-membered rings crossing each other six times. The metal ions are almost perfectly coplanar (Fig. 3b) and lie at the vertices of a regular hexagon (Fig. 3a). The role of the phenyl rings in directing the covalent bond-forming reactions used to close the circular helicate is apparent from the conformation and orientation of the ring-closing loops (Fig. 3c). The bipyridine-phenyl (NHC-C-C-CH) torsion angles are in the range 46–60° and the *ortho*-substitution pattern allows the hydrocarbon chain to connect the phenyl rings in a low-energy conformation with either *E* or *Z* olefin bonds (both are observed, with some

disorder, in an approximately a 2:1 *E:Z* ratio in the X-ray crystal structure). Within each circular helicate every $Fe(II)$ centre has the same coordination stereochemistry (Δ or Λ), with equal amounts of ($\Delta, \Delta, \Delta, \Delta, \Delta, \Delta$)-**4** and ($\Lambda, \Lambda, \Lambda, \Lambda, \Lambda, \Lambda$)-**4** present in the unit cell.

A PF_6^- anion (which remains despite the sodium tetraphenylborate solution used to promote the slow formation of the single crystal) lies at the centre of the two interlocked rings, oriented such that the fluorine atoms point towards the 12 electron-poor aromatic CH^1 protons that line the walls of the Star of David cavity ($CH^1 \cdots F$ distances, 1.88–2.43 Å). The remaining anions in the crystal structure, probably all tetraphenylborate ions, are disordered over several locations and orientations.

The Star of David $[2]$ catenate was demetallated by treatment of an acetonitrile solution of $[4](PF_6)_{12}$ with aqueous tetrasodium ethylenediaminetetraacetate (Na_4EDTA) (Fig. 4a); the loss of the reddish-purple colour indicates the removal of iron(II) from the bipyridine sites of **4**. Two compounds were isolated by size-exclusion chromatography. The major product (60%) was characterized as the demetallated Star of David $[2]$ catenand **5** (the 1H NMR spectrum is shown in Fig. 2e and the ESI-MS in Fig. 4c). To our surprise, the minor product (19%) was found to have a molecular mass equal to half that of **5**, and was determined to be the unlinked macrocycle **6**. ESI-MS of the pristine $[4](PF_6)_{12}$ starting material (Fig. 4b) showed no traces of circular helicates with incomplete ring closure and so it may be that contamination with trace (but clearly highly active, even in acetonitrile) ruthenium species from the RCM reaction is responsible for the ring opening of **5** and its rapid disassembly into non-interlocked species in the absence of iron(II) ions to hold the components together.

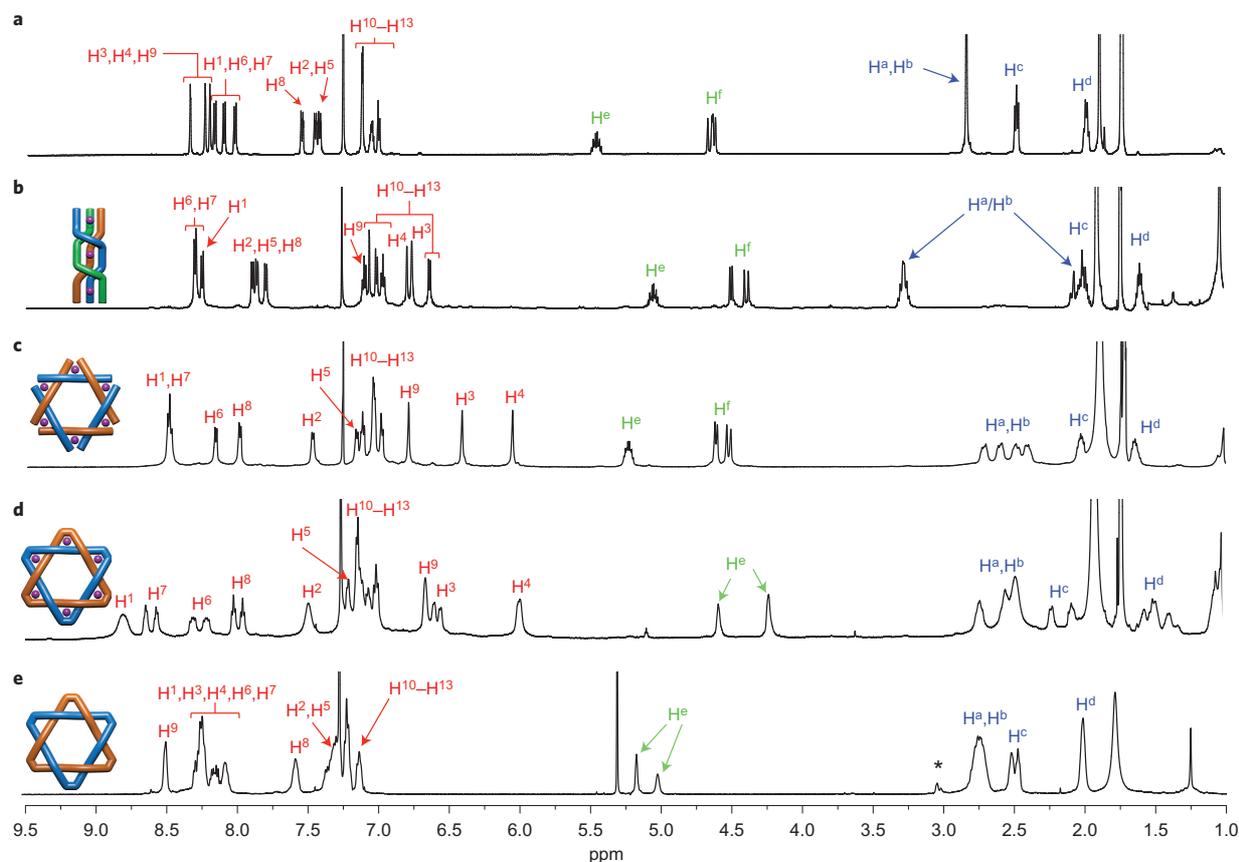


Figure 2 | ^1H NMR spectra (600 MHz, 298 K, $\text{CD}_3\text{CN}/\text{CDCl}_3$ (1:1) (a–d), CDCl_3 (e)) of uncoordinated ligand strand **1**, linear (**3**) and circular (**2**) helicates, and metallated (**4**) and demetallated (**5**) Star of David [2]catenanes. **a**, Ligand **1**. **b**, Linear triple helicate $[\mathbf{3}](\text{PF}_6)_6$. **c**, Cyclic hexameric helicate $[\mathbf{2}](\text{PF}_6)_{12}$. **d**, Star of David [2]catenane $[\mathbf{4}](\text{PF}_6)_{12}$. **e**, Demetallated Star of David [2]catenane **5** (the impurity marked * is caused by the presence of a small amount of the unlinked macrocycle **6**). The signal assignments correspond to the labelling shown in Fig. 1. The chemical shift of H^1 in $[\mathbf{2}](\text{PF}_6)_{12}$ and $[\mathbf{4}](\text{PF}_6)_{12}$ varies according to purity and concentration, probably a result of the binding of anions and/or solvent in the electron-poor cavity of the circular helicate.

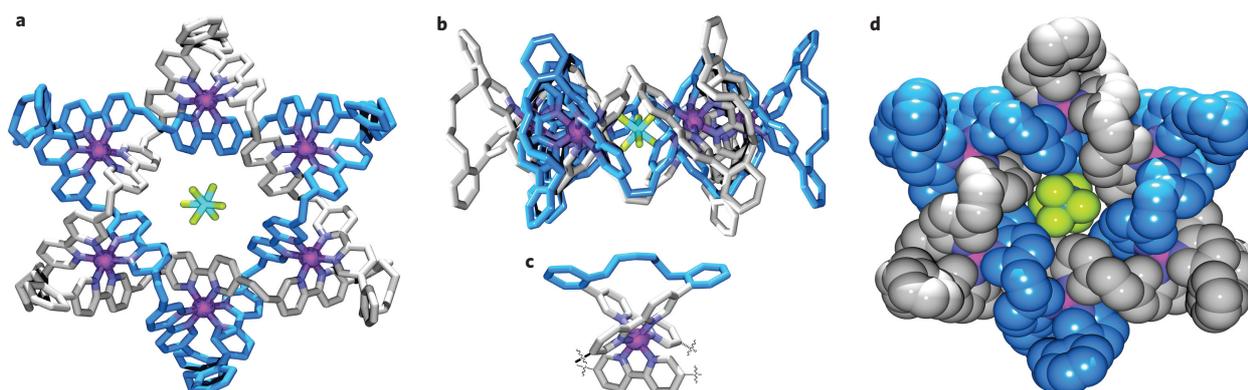


Figure 3 | X-ray crystal structure of Star of David catenane, $[\mathbf{4}](\text{PF}_6)(\text{Ph}_4\text{B})_{11}$. **a**, Viewed from above the central cavity of the circular helicate. **b**, Viewed in the plane of the $\text{Fe}(\text{II})$ cations. **c**, Cross-section showing the loop that connects two phenyl rings on a metal centre. **d**, Space-filling representation of the Star of David catenane. Hydrogen atoms, solvent molecules and anions, except for the central PF_6^- , are omitted for clarity. In **a**, **b** and **d**, the carbon atoms of one ring are coloured blue and of the other light grey, and in **c** the carbon atoms are in light grey for the bipyridine units and in blue for the connecting loop. In all structures: N, purple; Fe, pink; P, cyan; F, green. Fe–Fe distances (Å): 8.210(4), 7.705(4), 8.323(4), 8.210(4), 7.705(4), 8.323(4); Fe–Fe–Fe angles (°): 122.19(4), 120.39(5), 115.44(5), 122.19(4), 120.39(5), 115.44(5). Bipyridine–phenyl ring (NHC–C–C–CH) torsion angles (°): 60(3), 55(2), 46(3), 60(3), 55(2), 46(3), 55(3), 56(2), 60(2), 55(3), 56(2), 60(2). CH^+F^- distances (Å): 2.43, 2.41, 2.13, 1.91, 1.88, 2.26, 2.41, 2.43, 2.13, 1.91, 1.88, 2.26. Crystallographic data and experimental details of the structural refinement of $[\mathbf{4}](\text{PF}_6)(\text{Ph}_4\text{B})_{11}$ are provided in the Supplementary Information. A fly-around video of the X-ray crystal structure is available (Supplementary Video 1).

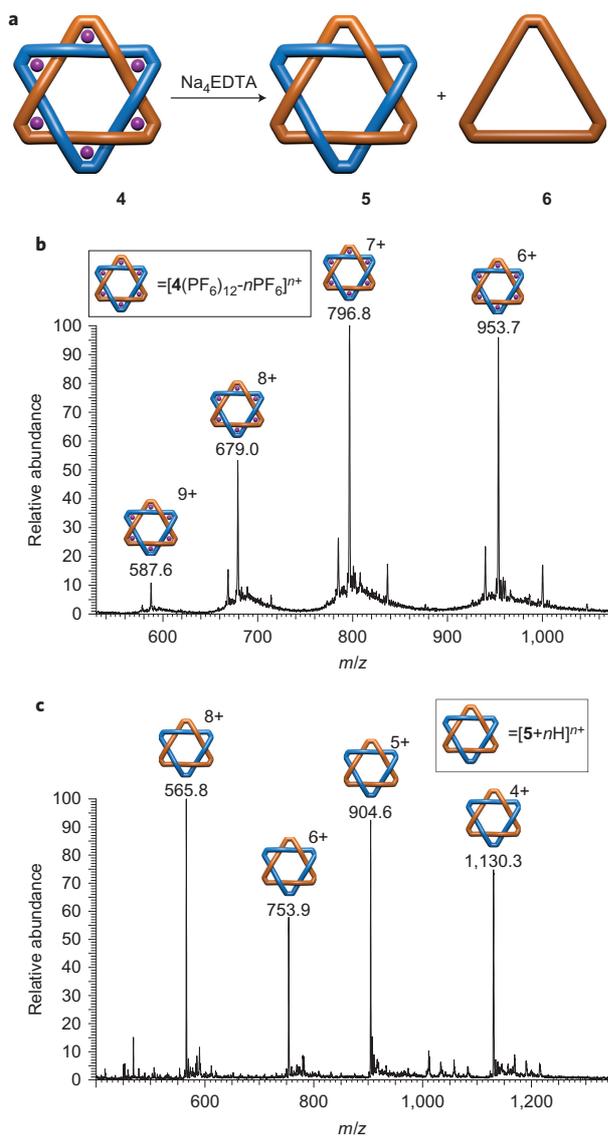


Figure 4 | Demetallation of the Star of David [2]catenane to form the wholly organic Star of David [2]catenane **5 and the unlinked macrocycle **6**.** **a**, Demetallation of the Star of David [2]catenane. Reaction conditions: H₂O/MeCN (1:1), 80 °C, four hours, resulting in **5** (60%) and **6** (38%). **b**, ESI-MS of the metal-containing Star of David catenane [4](PF₆)₁₂ with signals that correspond to the loss of various numbers of PF₆⁻ anions. Calculated peaks (*m/z*): 954.2 [M - 6PF₆]⁶⁺, 797.2 [M - 7PF₆]⁷⁺, 679.4 [M - 8PF₆]⁸⁺, 587.8 [M - 9PF₆]⁹⁺. **c**, ESI-MS of the demetallated Star of David catenane **5** with formic acid added to generate multiply protonated ions. Calculated peaks (*m/z*) 1,129.6 [M + 4H]⁴⁺, 903.8 [M + 5H]⁵⁺, 753.4 [M + 6H]⁶⁺, 565.3 [M + 8H]⁸⁺.

Conclusions

The 6₁¹ link is an iconic topology (as are the trefoil³⁷ and pentafoil³⁰ knots and Borromean rings¹²) that had resisted attempts to synthesize it in molecular form for more than two decades^{29,36}. The six-crossings framework of the Star of David catenane was generated by entwining six ligands around six octahedral iron(II) centres, with the size of the circular helicate promoted by the use of sulfate as the counteranion. The key to closing the open circular helicate lies in the structure of the extended ligand, designed to restrict the

conformational space accessed by the reactive terminal groups of each ligand prior to ring closure. The result is that the two triply interlocked 114-membered rings are assembled in two remarkably efficient steps: 75% yield for the 12-component self-assembly of the hexameric circular helicate; 92% yield for the six RCM reactions required for covalent capture of the interlocked structure.

Biology shows that topological complexity at the molecular level offers tremendous potential for achieving novel material properties⁵. The increasing understanding of how to combine complex supramolecular assembly processes with methods of directing covalent bond formation provides evermore effective synthetic routes to these elaborate, and often beautiful, molecular architectures.

Methods

Preparation of circular hexameric helicate [2](PF₆)₁₂. Solutions of **1** (50 mg, 64 μmol) in ethylene glycol (4 ml) and FeSO₄·7H₂O (18 mg, 64 μmol) in ethylene glycol (0.7 ml) were combined and heated at 170 °C in a sealed vial under argon for 24 hours with stirring. The resulting purple solution was cooled to room temperature, and a saturated solution of KPF₆ in methanol was added in excess until a precipitate formed. The solid was isolated by filtration onto Celite, and washed with water, methanol and dichloromethane. The resulting solid was taken up in acetonitrile, filtered and the solvent removed to give [2](PF₆)₁₂ as a red-purple solid (54 mg, 8.0 μmol, 75%). ¹H NMR (600 MHz, CD₃CN, 298 K) δ 8.83 (s, 2H, H¹), 8.70 (d, *J* = 8.2 Hz, 2H, H⁷), 8.37 (d, *J* = 8.2 Hz, 2H, H⁶), 8.29 (d, *J* = 8.0 Hz, 2H, H⁸), 7.74 (d, *J* = 7.5 Hz, 2H, H²), 7.48–7.21 (m, 10H, H², H¹⁰–H¹³), 7.01 (s, 2H, H³), 6.66 (s, 2H, H³), 6.28 (s, 2H, H⁴), 5.56–5.44 (m, 2H, H⁵), 4.84 (dd, *J* = 48.5, 13.7 Hz, 4H, H⁴), 2.79 (ddd, *J* = 50.5, 41.8, 13.3 Hz, 8H, H⁴, H⁵, H¹¹), 2.37–1.83 (m, 8H, H⁵, H⁴). ¹³C NMR (151 MHz, CD₃CN) δ 157.4 (N–C–C⁶), 157.0 (N–C–C⁷), 156.7 (N–C–C¹), 154.8 (C⁹), 154.6 (C³), 153.9 (C⁴), 142.2 (C⁸–C–C⁹), 141.6 (C⁸), 140.3 (C²), 140.2 (C²–C–C³), 139.9 (C⁵), 139.8 (C¹³–C–C⁵), 139.7 (C⁴–C–C⁵), 138.3 (C⁶), 136.0 (C¹⁰–C–C–C¹³), 131.2, 130.7, 130.5, 127.6 (C¹⁰–C¹³), 124.6 (C⁷), 123.9 (C⁶), 123.6 (C¹), 116.1 (C¹), 35.2 (C⁴), 32.7 (C⁵), 29.9, 29.8 (C³ and C⁸). Low-resolution (LR) ESI-MS *m/z* = 1,206.8 [M - 5PF₆]⁵⁺ requires 1,207.6; 981.6 [M - 6PF₆]⁶⁺ requires 982.2; 820.7 [M - 7PF₆]⁷⁺ requires 821.2; 700.1 [M - 8PF₆]⁸⁺ requires 700.4; 606.3 [M - 9PF₆]⁹⁺ requires 606.5; 531.1 [M - 10PF₆]¹⁰⁺ requires 531.4.

Preparation of the Star of David [2]catenane [4](PF₆)₁₂. A solution of [2](PF₆)₁₂ (25 mg, 3.7 μmol) in degassed anhydrous nitromethane (1.9 ml) was added to an oven-dried flask equipped with a stirrer bar under argon. The Hoveyda–Grubbs second-generation catalyst (H₂IMes)(Cl)₂RuCH(o-*o*-PrC₆H₄) (H₂IMes, 1,3-dimesitylimidazolinedi-2-ylidene) (2.3 mg, 3.7 μmol, 17 mol% with respect to ligand **1**) in degassed anhydrous dichloroethane (1.9 ml) was added and the reaction heated to 60 °C for 24 hours with stirring. After cooling to room temperature, the catalyst was quenched with excess ethyl vinyl ether (0.4 ml) and stirred for 30 minutes. The solvent was removed under reduced pressure and the resulting solid sonicated in chloroform for 15 minutes, filtered onto Celite, washed thoroughly with fresh chloroform and taken up in acetonitrile. Saturated aqueous KPF₆ was then added to the solution until a precipitate formed, which was again filtered onto Celite, washed with water, methanol and chloroform, and taken up in acetonitrile and filtered. The solvent was removed to afford [4](PF₆)₁₂ as a red-purple solid (23 mg, 3.4 μmol, 92%). ¹H NMR (600 MHz, CD₃CN, 298 K) δ 8.89 (br-s, 2H, H¹), 8.77 (dd, *J* = 43.3, 8.1 Hz, 2H, H⁷), 8.44 (dt, *J* = 49.9, 9.6 Hz, 2H, H⁶), 8.28 (dddd, *J* = 42.6, 8.3, 6.3, 1.9 Hz, 2H, H⁸), 7.72 (br-s, 2H, H²), 7.55–7.23 (m, 10H, H², H¹⁰–H¹³), 6.93 (s, 2H, H³), 6.84 (d, *J* = 22.8 Hz, 2H, H³), 6.24 (s, 2H, H⁴), 4.68 (d, *J* = 192.7 Hz, 2H, H⁴), 2.84 (m, 8H, H⁴, H⁵), 1.88–1.07 (m, 4H, H⁵, H⁴). ¹³C NMR (151 MHz, CD₃CN) δ 157.4, 157.3 (N–C–C⁶), 157.0, 156.9, 156.8 (N–C–C⁷, N–C–C¹), 155.2 (C³, C⁹), 154.2 (C⁴), 142.5 (C⁸), 142.4 (C⁸–C–C⁹), 142.2 (C⁸), 142.1 (C⁴–C–C⁵), 140.4 (C¹³–C–C⁵), 140.2 (C²–C–C³), 139.9 (C², C⁵), 136.5 (C¹⁰–C–C–C¹³), 131.7, 131.0, 130.7, 130.4 (C¹⁰/C¹¹/C¹²/C¹³), 129.8, 129.4 (C⁶), 127.8, 127.4 (C¹⁰/C¹¹/C¹²/C¹³), 124.5, 124.0 (C⁷), 123.7 (C¹, C⁹), 36.7 (C⁴), 33.8 (C⁵), 29.9 (C³, C⁸). LRESI-MS *m/z* = 1,502.8 [M - 4PF₆]⁴⁺ requires 1,503.8; 1,173.3 [M - 5PF₆]⁵⁺ requires 1,174.0; 953.7 [M - 6PF₆]⁶⁺ requires 954.2; 796.8 [M - 7PF₆]⁷⁺ requires 797.2; 679.0 [M - 8PF₆]⁸⁺ requires 679.4; 587.6 [M - 9PF₆]⁹⁺ requires 587.8.

Assignments for the proton and carbon NMR spectra correspond to the labelling shown in Fig. 1. Further information on the synthesis and characterization of all the compounds, including the synthetic building blocks used to generate **1** and the demetallated Star of David (**5**), is provided in the Supplementary Information.

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Author contributions

A.J.S. carried out the synthesis and characterization studies, helped plan the experiments and write the manuscript. R.G.P. solved the crystal structure. D.A.L. helped plan the experiments and write the manuscript.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.A.L.

Competing financial interests

The authors declare no competing financial interests.