



Controlling the Shape and Chirality of an Eight-crossing Molecular Knot

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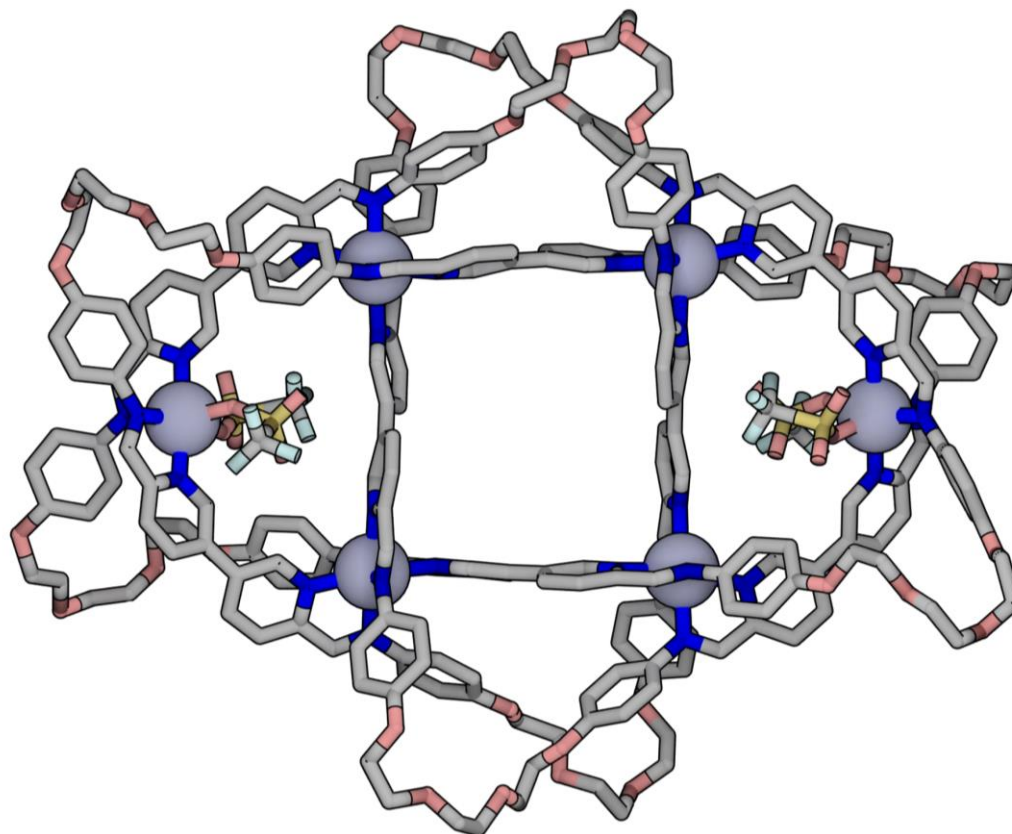
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Highlights:

- We show that subcomponent self-assembly can generate a complex knotted architecture with eight crossing points, with peripheral metals centres enforcing additional nugatory crossings.
- We find that the metal-organic molecular knot can be reduced and demetallated, to form a single, continuous, knotted organic loop of 240 atoms, which relaxes to a more symmetric conformation.
- We show that we can control the topological chirality of this molecular knot, enabling its diastereoselective synthesis.

The Bigger Picture:

Knots are ubiquitous in the macroscopic world, with uses ranging from tying shoelaces to fishing, and they transform the properties of that in which they are tied. Knots are similarly found at the nanoscale, for example in proteins and DNA, and also in man-made polymers. These molecular entanglements likewise control the properties of the molecules in which they are tied - chain breakage in polymers occurs most readily at the knotted point, and knotting in biomolecules can enhance stability. Herein we describe the formation of a molecular knot with eight crossing points, via one-pot self-assembly from a pair of simple starting materials and a single metal salt. Further, as the 8_{19} knot that we form is intrinsically topologically chiral, we show that we can diastereoselectively form the knot by using an enantiopure building block, allowing us to use point chirality to control the topological chirality of this complex architecture.

**Graphical Abstract:****Summary:**

The knotting of biomolecules impacts their function, and enables them to carry out new tasks. Likewise, complex topologies underpin the operation of many synthetic molecular machines. The ability to generate and control more complex knotted architectures is essential to endow these machines with more advanced functions. Here we report the synthesis of a molecular knot with eight crossing points, consisting of a single organic loop woven about six templating metal centres, via one-pot self-assembly from a simple pair of dialdehyde and diamine subcomponents and a single metal salt. The structure and topology of the knot were established by NMR spectroscopy, mass spectrometry and X-ray crystallography. Upon demetallation, the purely organic strand relaxes into a symmetric conformation, whilst retaining the topology of the original knot. This knot is topologically chiral, and may be synthesised diastereoselectively through the use of an enantiopure diamine building block.

Introduction:



Knots are one of the oldest technologies, having been used for thousands of years to transform the properties of the materials in which they are tied.¹ At the molecular level, knots are found in biology in proteins and DNA,^{2,3} and form spontaneously in sufficiently long polymer chains.^{4,5} Chain breakage in these polymer systems occurs most readily at the knotted point,⁶ whereas knotting together of proteins in the HK97 viral capsid renders it more robust.⁷ Knotting at the molecular level thus has major effects upon material properties.^{8,9} Since Sauvage's first full characterisation of synthetic knotted molecules three decades ago,¹⁰ the beauty of these woven architectures has attracted chemists,¹¹ leading to recent breakthroughs in the synthesis of complex, highly symmetric, knots,^{12,13,14,15,16,17,18} and to investigations of their functions.^{19,20}

To date, synthetic routes to molecular knots and links have focussed on the preparation of highly symmetric knots with few crossing points, such as the three-crossing trefoil knot.^{21,22,23,24,25,26,27,28,29,30} Symmetrical higher order knots and links with up to nine crossing points have recently been prepared,³¹ often based on the circular helicate approach pioneered by the Leigh group.^{32,33} These increasingly complex knots have been used to control catalysis,^{19,34} and they show strong and specific anion binding.³⁵ Many molecular knots are topologically chiral, possessing handedness that arises from the way in which their strands are woven together. Given that chirality is critical to function in nature and technology,^{36,37} the control of chirality in topologically complex molecular architectures is anticipated to enable progressively more complex applications.^{38,39} Topologically stereoselective synthesis has been achieved for trefoil knots,^{40,41} and for knots formed from combinations of trefoil knots,^{28,31} but no route to control the topological chirality of higher covalent knots has yet been reported.

Here we report the single-step synthesis of a molecular knot with eight crossing points, an 8_{19} knot.¹² This knot was formed in a single step by the subcomponent self-assembly of a diamine, a dialdehyde, and a metal salt. Upon reduction and demetallation, the knot relaxed into a higher-symmetry configuration. Furthermore, embedding remote stereocentres into the diamine subcomponent enabled control over the topological chirality of the 8_{19} knot product.

Results and Discussion:

The 8_{19} molecular knot reported herein consists of a single organic molecular strand which weaves a continuous path about six templating metal centres. This entangled molecule can be prepared through either a single-step process, or in stepwise fashion from a pre-assembled grid in enhanced yield.

Subcomponent **A** (Fig. 1) has been shown to self-assemble with *p*-toluidine and different metal salts to produce a family of structurally distinct supramolecular architectures.^{42,43,44} One of these is the M_6L_8 (where $M = Co^{II}, Ni^{II}, Zn^{II}$) extended circular helicate **1** (Fig. 1, Zn-**1**). In **1**, eight bis-bidentate ligands weave about the six metal centres. The use of $M(OTf)_2$ in these systems is essential, as one triflate anion occupies the central cavity of the extended circular helicate and templates this architecture over alternative structures.

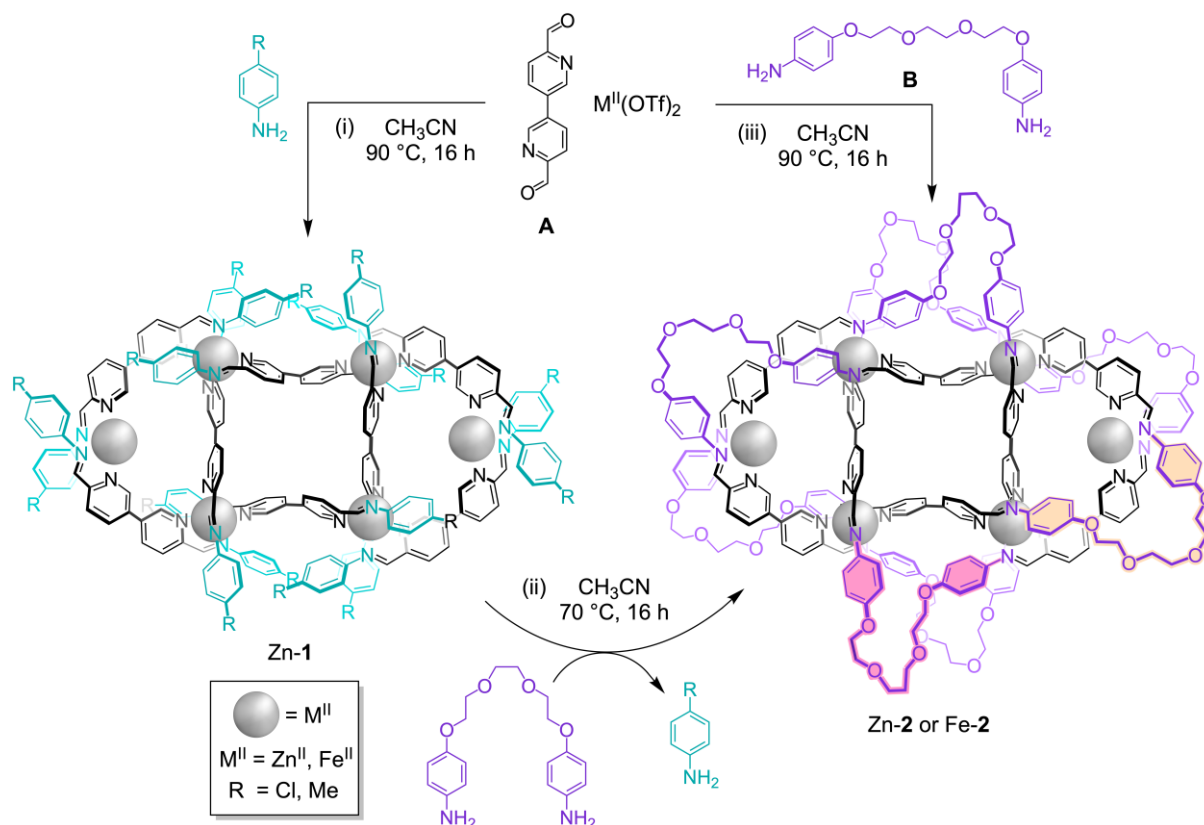


Figure 1. Synthesis of an eight-crossing molecular knot

(i) Treatment of dialdehyde **A** (8 equiv) with a mono-aniline (16 equiv) and either $\text{Zn}(\text{OTf})_2$ or $\text{Fe}(\text{OTf})_2$ (6 equiv) led to the formation of the framework of extended circular helicate **1**. Eight-crossing molecular knot **2** formed (ii) *via* aniline exchange from **1**, or (iii) directly from subcomponents **A** and **B** together with the metal template. Exemplars of two types of dianiline linkage are highlighted in pink and orange for clarity. Coordinated triflate anions are omitted.

Within **1**, certain pairs of aniline residues are spatially closer together than others. Noting that each of these proximal anilines were attached to different metal centres, we reasoned that linking them might yield an entangled, topologically complex species. Molecular models suggested that optimal linker length requirements would be met by the triethylene glycol chain of bis-*para*-substituted dianiline **B**.

The reaction of dialdehyde **A** (8 equiv) with dianiline **B** (8 equiv) and zinc(II) trifluoromethanesulfonate (triflate, TfO^-) (6 equiv) in acetonitrile at 90 °C thus produced **Zn-2**, with NMR and ESI-MS analyses consistent with the structure shown in Fig. 1 (Supplemental Information Section 3).

Preparing **Zn-2** directly from its subcomponents (Fig. 1, pathway (iii)) led to the formation of a small amount of insoluble precipitate, which we infer to be kinetically-trapped polymeric material. We therefore hypothesised that a stepwise preparation (Fig. 1, pathway (ii)) *via* aniline exchange from extended circular helicate **Zn-1**, incorporating electron-poor 4-chloroaniline, might avoid the formation of these side products.⁴⁵ The isolated yield of **Zn-2** was thus found to increase from 72%, for direct assembly, to 92%, using the stepwise approach from the grid **Zn-1** formed from 4-chloroaniline (Supplemental Information Section 4).



Slow diffusion of diisopropyl ether into an acetonitrile solution of Zn-**2** provided yellow crystals suitable for analysis by single-crystal X-ray diffraction. The solid-state structure unambiguously confirmed that the topology of **2** corresponds to an 8_{19} knot. The organic ligand of the knot weaves a continuous path 240 atoms long around each of the six metal centres, crossing itself eight times. The eight triethylene glycol linkers of dianiline **B** are in two distinct environments (for further details, see Supplemental Information Section 3), which are highlighted in pink and orange in Fig. 1.

The six metal centres of Zn-**2** were found to be approximately coplanar. The four central zinc(II) cations are bound by three pyridyl-imine groups, while the peripheral zinc(II) centres are coordinated to two such units, as well as two triflate anions, which together satisfy an octahedral coordination environment. Both enantiomers of Zn-**2** were observed in the crystal, linked by a centre of inversion.

A similar result was obtained from the reaction of dialdehyde **A** (8 equiv) with dianiline **B** (8 equiv) and iron(II) triflate (6 equiv) in acetonitrile, yielding Fe-**2** (Supplemental Section 5). Fe-**2** was shown to possess the same topology as Zn-**2** by X-ray crystallography (Supplemental Information Section 13). As in the zinc(II) congener, the octahedral coordination spheres of the two peripheral iron(II) centres of Fe-**2** are each completed by two triflate anions. The low ligand field strength of triflate stabilises the high-spin state of these peripheral iron(II) centres, as reflected in longer Fe-N bond lengths of 2.15 ± 0.04 Å. This high-spin character caused Fe-**2** to exhibit paramagnetism, as seen in its ^1H NMR spectrum (Supplemental Information Section 5). In contrast, the inner iron(II) centres adopted a low-spin state due to the higher ligand field strength of the three pyridyl-imine groups bound to each, with shorter Fe-N bond-lengths of 1.98 ± 0.03 Å.⁴⁵

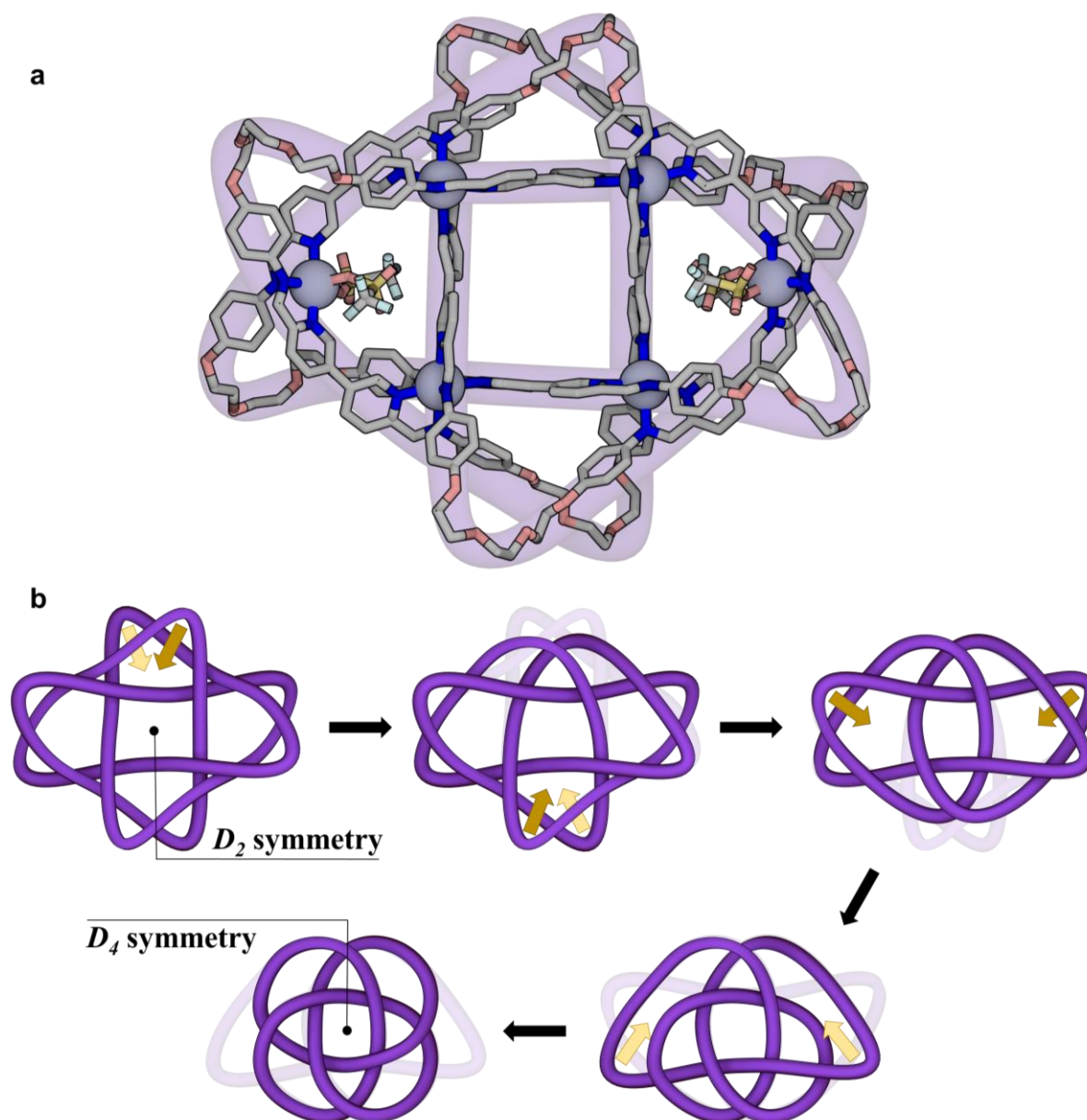


Figure 2. X-ray crystal structure and topology of molecular knot **2**

a. X-ray crystal structure of Zn-**2**. Hydrogen atoms, disorder, non-coordinated anions and solvent are omitted for clarity. **b.** Schematic representation of the transformation of D_2 -symmetric eight-crossing knot **2** into its topologically equivalent, D_4 -symmetric form. Gold and yellow arrows indicate deformation of the knot from its low-symmetry D_2 configuration into its D_4 symmetric form, with gold arrows representing the four conceptual Reidemeister type II moves which reduce the number of apparent crossing points from 16 to eight.

The Leigh group have reported a topologically-equivalent eight-crossing knot, which possesses D_4 symmetry.^{12,46} In contrast, the metallated molecular knots Zn-**2** and Fe-**2** exhibit D_2 symmetry (Supplemental Section 13). Knot **2** appears on first inspection to possess additional crossing points, with 16 seen in total (Fig. 2b). Eight of these crossing points are nugatory: loops may be moved past each other so as to effect their removal, without breaking and re-joining



the organic strand (Fig. 2b and Video S1). These manipulations are referred to as Reidemeister moves (Supplemental Information Section 6), which transform a knot or link into a new representation without altering its topology.¹¹ Every knot can be deformed using such moves into a configuration which exhibits the minimal number of possible crossing points. Fig. 2b shows four Reidemeister moves which transform **2** into its simplest representation, that of a symmetric torus knot (Fig. 2b, Supplemental Information Section 6).

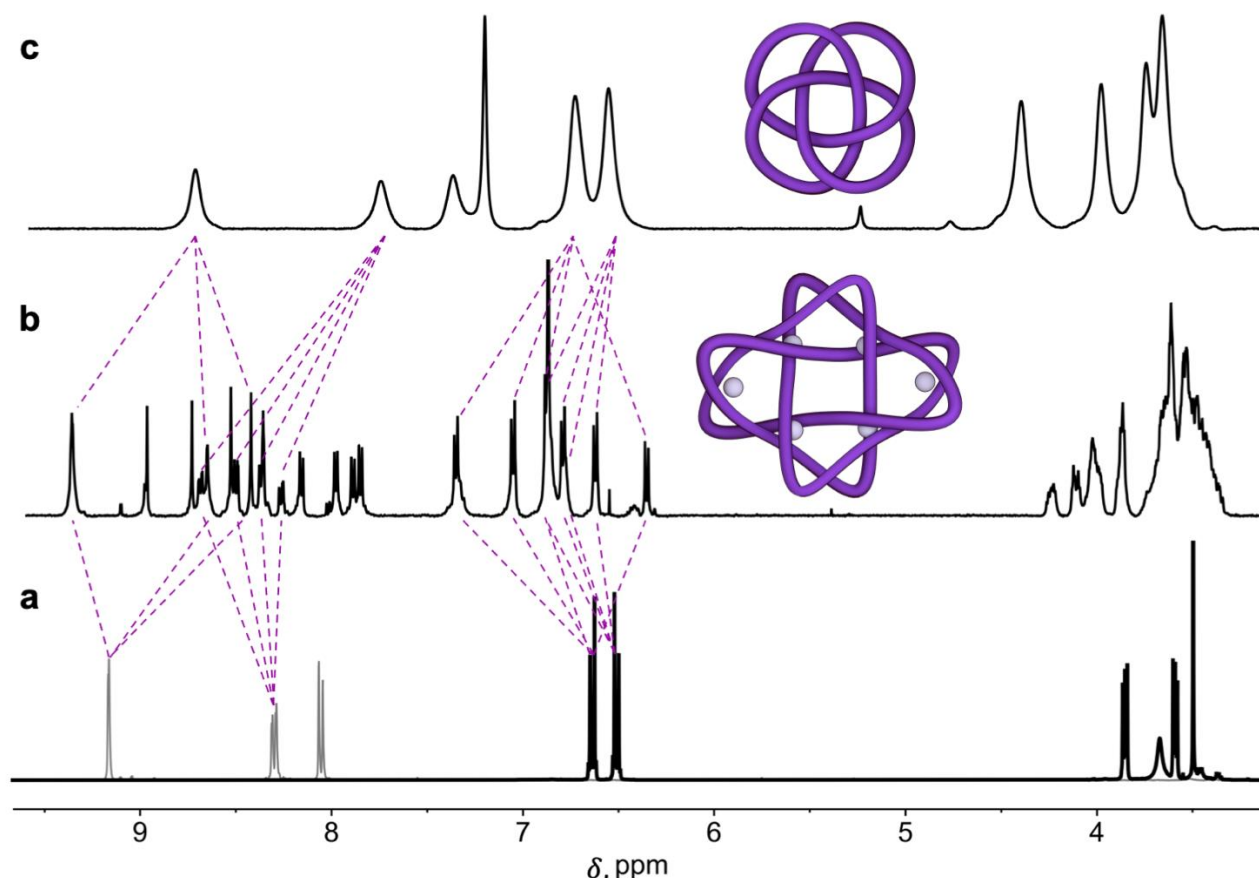


Figure 3. ^1H NMR spectra of knots **Zn-2** and **3**

Partial ^1H NMR spectra of **a.** superimposed spectra of dialdehyde **A** (grey) and dianiline **B** (black) with no transition metal salt added (500 MHz, 298 K, CD_3CN), **b.** metallated molecular knot **Zn-2** (500 MHz, 298 K, CD_3CN) and **c.** demetallated and reduced, purely-organic, knot **3** synthesised from **Fe-2** (500 MHz, 298 K, CDCl_3).

Such a symmetric conformation was adopted by fully organic, non-labile eight crossing knot **3**, which was prepared through the reduction and demetallation of **Fe-2** (Fig. 3). Reduction of **Fe-2** with $\text{BH}_3 \cdot \text{THF}$ in an acetonitrile:methanol (5:1, v:v) mixture led to the transformation of the labile imine linkages holding the parent structure together into fixed secondary amines,⁴⁷ thus leading to the formation of the fully organic knot **3**, as confirmed by mass spectrometry (Supplemental Information Section 8). In contrast to the 24 aromatic ^1H NMR resonances observed for **Zn-2** (Fig. 3b), only five were observed for **3** (Fig. 3c). The constitutionally equivalent sections of knot **3** thus reside in magnetically



equivalent environments.^{12,46} Variable temperature NMR experiments showed this equivalence to persist over a temperature range of 25 °C – –50 °C (Supplemental Information Section 8).

The 8_{19} knot is inherently topologically chiral, a property resulting from its spatial connectivity. When achiral subcomponents were incorporated, the expected racemic mixture of the two knot enantiomers was obtained. These topological enantiomers could be distinguished by adding the tetrabutylammonium salt of Lacour's Δ -TRISPHAT to Zn-**2**,⁴⁸ which led to a separate ^1H NMR spectrum for each enantiomer (Supplemental Information Section 9). We hypothesised that incorporating remote stereocentres into the dianiline subcomponent would lead to the formation of a knot having a single topological handedness.^{25,49} We therefore synthesised enantiopure dianilines **C**-(1*R*,2*R*) and **C**-(1*S*,2*S*) (Supplemental Information Section 10). These dianilines provide a similar-length chain to that of dianiline **B**. The reaction of dialdehyde **A** (8 equiv) with dianiline **C**-(1*R*,2*R*) (8 equiv) and iron(II) triflate (6 equiv) resulted in the formation of molecular knot Fe-**4**-(1*R*,2*R*), as evidenced by low and high resolution ESI mass spectrometry (Figures S44 and S45). The paramagnetic ^1H NMR spectrum of Fe-**4**-(1*R*,2*R*) (Figure S41) was similar to that of Fe-**2**, and to that obtained in the case of Fe-**4**-(1*S*,2*S*), formed from **C**-(1*S*,2*S*) (Supplemental Information Section 11, Figure S43).

Circular dichroism (CD) spectroscopy was used to gauge the stereoselectivity of the formation of knots Fe-**4**-(1*R*,2*R*) and Fe-**4**-(1*S*,2*S*). CD spectra show bands of equal and opposite intensity for Fe-**4**-(1*R*,2*R*) and Fe-**4**-(1*S*,2*S*). Furthermore, intense bisignate MLCT bands centred at 581 nm were observed in the CD for each (Fig. 4b). Equal and opposite signals centred at 581 nm were recorded for Fe-**4**-(1*R*,2*R*) and Fe-**4**-(1*S*,2*S*). This confirms the presence of non-racemic stereogenic metal centres, and indicates that Fe-**4**-(1*R*,2*R*) contains Δ iron centres, and Fe-**4**-(1*S*,2*S*) Λ .^{50,51,52} Only one set of peaks were apparent by ^1H NMR spectroscopy (Supplemental Information Section 11). These observations indicated that the stereochemical information of the chiral cyclohexane residues was effectively communicated to the metal centres of the molecular knot during self-assembly, thereby resulting in the favoured formation of one knot stereoisomer. Whilst it is clear that stereoinduction is strong (reinforced by the ^1H NMR of the diamagnetic Zn-**4** knot, *vide infra*, and Figures S47 and S48), we cannot precisely quantify the extent of stereoinduction in this system. Stereochemical information transmission thus occurred efficiently over a path of at least 10 atoms in order to dictate the handedness of the metal centres, with the 16 stereogenic units acting in concert to exert strong control.

Zinc(II)-templated molecular knots Zn-**4**-(1*R*,2*R*) and Zn-**4**-(1*S*,2*S*) were prepared by an analogous self-assembly process (Supplemental Information Section 12). ^1H NMR spectroscopy showed formation of one major diastereomer in each case (Supplemental Information Section 12). CD spectroscopy again revealed strong bands of equal and opposite intensity (Figure S57).

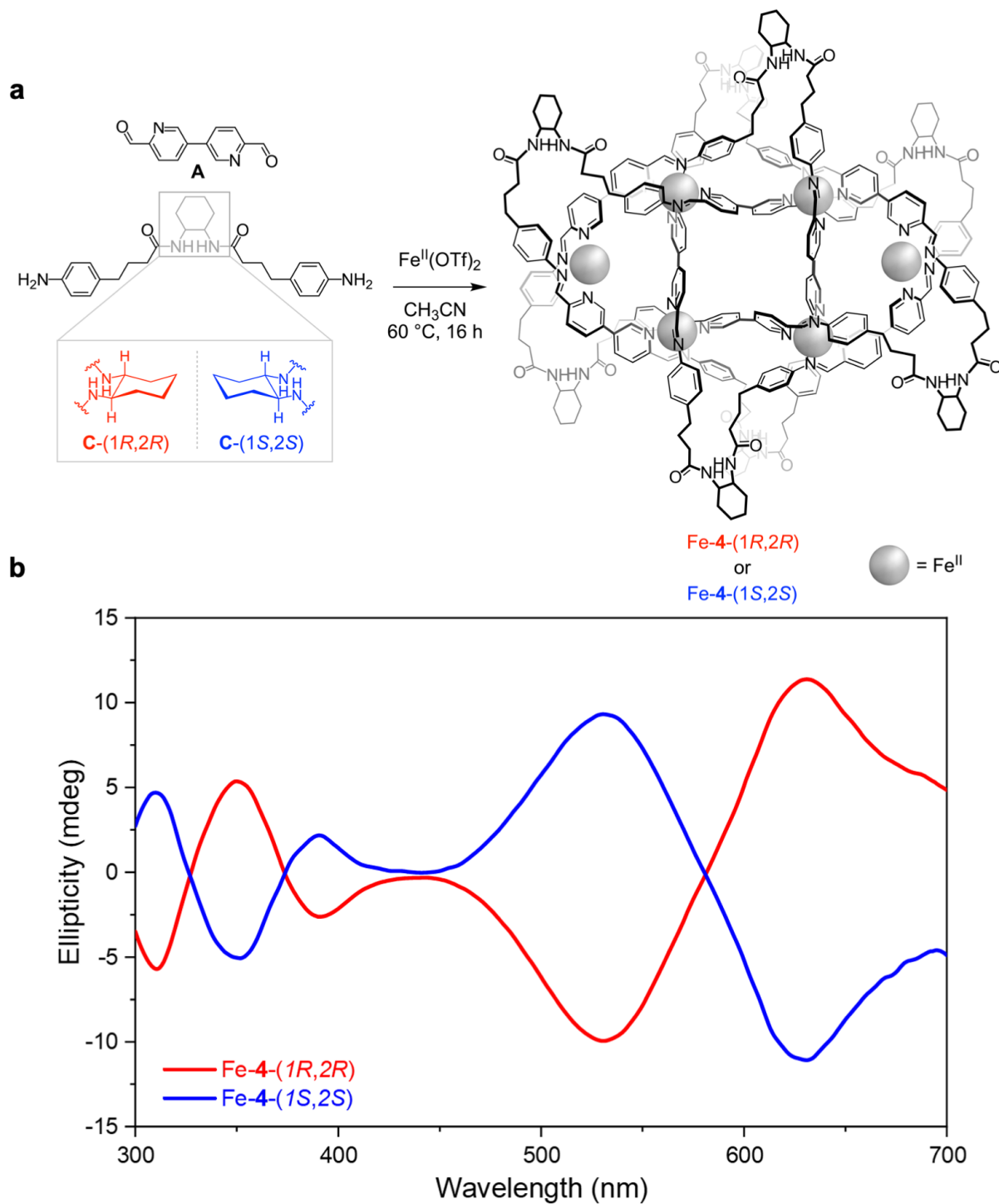


Figure 4. Diastereoselective self-assembly of an eight-crossing knot

a. Treatment of subcomponent **A** (8 equiv) with iron(II) triflate (6 equiv) and either **C-(1R,2R)** or **C-(1S,2S)** (8 equiv) led to the stereoselective synthesis of eight crossing knots **Fe-4-(1R,2R)** and **Fe-4-(1S,2S)**, respectively. **b.** CD spectra of **Fe-4-(1R,2R)** and **Fe-4-(1S,2S)** at 298 K in CH_3CN at the same concentration (10 μM).

Conclusion:



The successful synthesis and reductive demetallation of a metal-organic eight crossing point knot *via* a simple, one-pot, and high-yielding procedure highlights the power of subcomponent self-assembly in the formation of entangled species with complex topology.^{13,45,53} The ability to control the shape and geometric configuration of these entanglements, as well as their topological chirality, will enhance our ability to probe the fundamental effects of such entanglements on the molecular level. This will inform the development of nanoscale woven materials, molecular devices and future innovations in the field.

Experimental Procedures:

Preparation of [Zn-2](OTf)₁₂. 6,6'-Diformyl-3,3'-bipyridine **A** (3.56 mg, 16.8 μmol, 8 equiv), 4,4'-(((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))dianiline **B** (5.60 mg, 16.8 μmol, 8 equiv) and Zn(OTf)₂ (4.44 mg, 12.2 μmol, 6 equiv) were added to a small Schlenk flask (total volume 4 mL). CH₃CN (1 mL) was added along with a Teflon-coated magnetic stir-bar. The sealed Schlenk flask was sonicated for 10 minutes and left to stir at 90 °C for 16 hours. The light-yellow reaction mixture was allowed to cool to room temperature and was then filtered through a glass fibre filter (0.7 μm pore size). Addition of diisopropyl ether (2 mL) resulted in the precipitation of a yellow solid. The suspension was then centrifuged (10 min, 3000 RPM), the eluent decanted. Further diisopropyl ether (2 mL) was added, the powder was resuspended by sonication and then centrifuged. Again, the eluent was decanted. The residue was then dried *in vacuo* to afford the solid product as a light-yellow powder (9.9 mg, 72%). ¹H NMR (500 MHz, 298 K, CD₃CN) δ: 9.42 (s, 4H), 9.41 (s, 4H), 9.02 (s, 4H), 8.79 (s, 4H), 8.74 (dd, J = 8.4, 2.2 Hz, 4H), 8.71 (d, J = 2.1 Hz, 4H), 8.58 (s, 4H), 8.56 (dd, J = 8.0, 2.0 Hz, 4H), 8.48 (s, 4H), 8.43 (dd, J = 8.0, 2.3 Hz, 4H), 8.42 (s, 4H), 8.32 (dd, J = 8.4, 2.4 Hz, 4H), 8.22 (d, J = 8.3 Hz, 4H), 8.04 (d, J = 7.9 Hz, 4H), 7.95 (d, J = 8.3 Hz, 4H), 7.91 (d, J = 8.0 Hz, 4H), 7.41 (d, J = 8.7 Hz, 4H), 7.11 (d, J = 8.9 Hz, 8H), 6.94 (d, 8H, overlapped), 6.93 (d, overlapped, 8H), 6.93 (d, overlapped, 8H), 6.85 (d, J = 8.8 Hz, 4H), 6.68 (d, J = 8.9 Hz, 4H), 6.41 (d, J = 8.8 Hz, 4H), 4.32–3.40 (H, m, aliphatic, 96H). ¹³C NMR (125 MHz, 298 K, CD₃CN) δ: 164.9, 162.0, 161.2, 161.1, 160.5, 160.3, 160.1, 157.3, 150.4, 150.0, 149.3, 149.3, 147.9, 147.9, 147.6, 147.4, 146.8, 142.6, 141.9, 141.9, 140.4, 139.7, 139.4, 139.2, 138.9, 137.4, 137.3, 137.2, 136.7, 135.6, 131.2, 130.9, 130.9, 128.9, 125.7, 124.5, 124.0, 123.7, 118.2, 116.6, 116.1, 115.8, 73.3, 72.0, 71.4, 71.3, 71.2, 71.0, 70.3, 70.1, 70.1, 69.9, 69.5, 69.2, 68.8, 68.8, 68.7, 62.0.

Preparation of [Zn-4](OTf)₁₂. 6,6'-Diformyl-3,3'-bipyridine **A** (14.2 mg, 67.0 μmol, 8 equiv), **C**-(1*R*,2*R*) (29.5 mg, 66.1 μmol, 8 equiv) and Zn(OTf)₂ (18.4 mg, 49.0 μmol, 6 equiv) were added to a small Schlenk flask (total volume 25 mL). CH₃CN (8 mL) was added along with a Teflon-coated magnetic stir-bar. The sealed Schlenk flask was sonicated for 10 minutes and left to stir at 90 °C for 16 hours. The light-yellow reaction mixture was allowed to cool to room temperature and was then filtered through a glass fibre filter (0.7 μm pore size). The acetonitrile solution was concentrated under a stream of N₂ to a volume of 2 mL. Addition of diisopropyl ether (6 mL) resulted in the precipitation of a yellow solid. The suspension was then centrifuged (10 min, 3000 RPM), the eluent decanted. Further diisopropyl ether (2 mL) was added, the powder was resuspended by sonication and then centrifuged. Again, the eluent was decanted. The residue was then dried *in vacuo* to afford the solid product as a fine light-yellow powder (44 mg, 73%). ¹H NMR (500 MHz, 298 K, CD₃CN) δ: 9.48 (d, J = 2.1 Hz, 4H), 9.40 (d, J = 2.1 Hz, 4H), 9.11 (s, 4H), 8.93 (s, 4H), 8.75 (s, 4H), 8.72 (dd, J = 7.9, 2.1 Hz, 4H), 8.70 (dd, J = 7.9, 2.1 Hz, 4H), 8.57 (s, 4H), 8.49 (s, 4H), 8.44 (dd, J = 8.0, 2.1 Hz, 4H), 8.33 (dd, J = 8.3, 2.2 Hz, 4H), 8.28 (d, J = 8.3 Hz, 4H), 8.11 (d, J = 2.2 Hz, 4H), 8.05 (d, J = 2.2 Hz, 4H), 8.02 (d, J = 2.2 Hz, 4H), 7.86 (d, J = 8.0 Hz, 4H),



7.76 (d, $J = 8.6$ Hz, 4H, amide NH), 7.36 (d, $J = 8.3$ Hz, 8H), 7.22 (d, $J = 8.2$ Hz, 8H), 7.12 (d, $J = 8.2$ Hz, 8H), 7.10 (d, $J = 8.4$ Hz, 8H), 6.96 (d, $J = 8.5$ Hz, 8H), 6.84 (d, $J = 8.0$ Hz, 8H), 6.79 (d, $J = 6.5$ Hz, 4H, amide NH), 6.69 (d, $J = 8.7$ Hz, 8H), 6.64 (d, $J = 6.7$ Hz, 4H, amide NH), 6.37 (d, $J = 8.1$ Hz, 8H, amide NH), 6.09 (d, $J = 8.3$ Hz, 8H), 3.86–3.76 (4H, m), 3.65–3.53 (16H, m), 2.92–2.83 (4H, m), 2.66–2.39 (32H, m), 2.37–2.29 (4H, m), 2.37–2.29 (4H, m), 1.85–1.62 (56H, m), 1.42–1.14 (56H, m). ^{13}C NMR (125 MHz, 298 K, CD_3CN) δ : 174.0, 173.8, 173.5, 173.2, 172.8, 165.5, 163.2, 161.8, 158.3, 150.2, 149.9, 148.8, 147.6, 147.5, 147.1, 147.0, 146.7, 146.0, 145.5, 144.8, 144.5, 144.1, 143.9, 143.9, 143.7, 142.8, 142.7, 142.5, 142.0, 140.7, 138.9, 137.5, 136.8, 136.1, 131.7, 131.6, 131.3, 131.2, 130.7, 130.4, 130.1, 129.9, 128.9, 123.9, 122.5, 122.3, 122.2, 55.4, 54.2, 53.7, 52.1, 37.6, 36.8, 36.5, 36.3, 36.2, 35.7, 35.5, 35.0, 34.4, 34.1, 33.7, 33.4, 33.1, 32.9, 32.7, 28.8, 28.7, 28.5, 26.6, 26.0, 25.7, 25.6, 25.5. Not all of the expected peaks in the aliphatic region of the ^{13}C NMR spectrum could not be resolved due to overlapping signals.

Complete assignment of both $[\text{Zn-2}](\text{OTf})_{12}$ and $[\text{Zn-4}](\text{OTf})_{12}$ are available in the Supplemental Information. Details for the synthesis of both $[\text{Fe-2}](\text{OTf})_{12}$ and $[\text{Fe-4}](\text{OTf})_{12}$ are available in the Supplemental Information.

Preparation of 3. To a stirred solution of $[\text{Fe-2}](\text{OTf})_{12}$ (62 mg, 10 μmol , 1 equiv) in MeCN/MeOH (5/1, v/v, 12 mL total volume) at room temperature was added $\text{BH}_3 \cdot \text{THF}$ (1 M, 480 μL , 480 μmol , 3 equiv/imine). The mixture was stirred for 10 minutes as the colour of the solution changed from deep green to dark brown. CH_2Cl_2 (10 mL) and ethylenediamine (18 μL , 0.27 mmol, 4.5 equiv/ Fe^{II}) were then added and the mixture was stirred for 10 minutes. The resulting suspension was poured in 30 mL H_2O and the mixture was extracted with 10 $\times$ 5 mL CH_2Cl_2 (note: the emulsions were broken mechanically). The combined organic layers were filtered on cotton covered with sand, then solvents were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 , filtered over Celite and dried *in vacuo* affording the reduced and demetallated knot **3** (25.4 mg, 6.19 μmol , 62%). ^1H NMR (500 MHz, 298 K, CD_3CN) δ : 8.72 (1H, br), 7.80 (1H, br), 7.43 (1H, br), 6.79 (2H, br), 6.57 (2H, br), 4.46 (2H, br), 4.04 (2H, br), 3.81 (2H, br), 3.68 (2H, br). ^{13}C NMR (125 MHz, 298 K, CD_3CN) δ : 159.0, 151.6, 147.6, 142.3, 135.1, 132.9, 121.9, 116.2, 114.4, 71.0, 70.1, 68.3, 50.2.

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Author Contributions

JPC and JRN conceived the project. JPC, CTM, JLG and RL performed the experiments and analysed the data. TKR collected the X-ray data and refined the structures. All authors discussed the results and edited the manuscript.



Additional Information

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, under the deposition numbers 2000486 (Zn-2) and 2000487 (Fe-2). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Correspondence and requests for materials should be addressed to JRN.

Competing financial interests

The authors declare no competing financial interests