In the realm of supramolecular chemistry, a small number of intricately interwoven structures that bridge the boundaries between art and science have been reported. These motifs, which typically form on the nanometre scale, display both considerable beauty and complexity. However, the generation of new topologies of this type has remained a very significant synthetic challenge. Here, we describe the synthesis of a discrete highly intertwined metallosupramolecular assembly based on a universal 3-ravel motif—a topology as yet unprecedented in supramolecular chemistry. The exotic, 20-component, $[\text{Fe}_{8}\text{L}_{12}]$ ravel entanglement may be considered as a ‘branched knot’, with individual molecules displaying either left- or right-handed chirality. The formation of this cluster was demonstrated by single-crystal and powder X-ray diffraction. The arrangement is stabilized by a favourable combination of $\pi$–$\pi$ interactions and Nature’s tendency to minimize voids in molecular architectures.

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Throughout human history aesthetically pleasing objects and structures have been admired as art, architecture or simply as attractive ornamental designs. In contrast, it is only since the rise of modern chemistry that it has become increasingly possible to parallel this aspect of the macro-world by constructing intricate structures and designs at the molecular level—in a few instances corresponding to attractive motifs that are not without artistic nuances. For example, over the past few decades considerable progress has been made in generating intertwined topologies\(^1\)–\(^3\) that include molecular trefoil knots\(^4\), Borromean rings\(^5\)–\(^8\), Solomon knots\(^9\) and mechanically interlinked structures of the catenane and rotaxane type\(^1\). Such intriguing architectures have been achieved using a variety of strategies, often involving significant practical and intellectual challenges, that are typically based on either metal template control or on the use of non-covalent interactions to direct the assembly process\(^1\)–\(^7\). In particular instances structures of this type have also inspired the construction of simple molecular machines\(^9\)–\(^11\).

In recent work, our group has used aryl-linked bis-\(\beta\)-diketone domains (replacing the rigid phenylene or biphenylene spacers used in our previous studies)\(^1\). We also report the results of an investigation of its use for constructing new metal-containing supramolecular architectures. The introduction of limited flexibility into supramolecular building blocks, although tending to reduce the predictability of the resulting assemblies, can nevertheless result in the generation of new molecular topologies that are not able to be achieved without such flexibility\(^1\)–\(^3\). Indeed, the interaction of LH\(_1\) with ferric chloride generates a discrete highly intertwined metallosupramolecular assembly based on a universal 3-ravel motif (Fig. 1a)—a molecular architecture so far unprecedented in supramolecular chemistry; trefoil knot and Borromean rings topologies are also illustrated in Figure 1bc for comparison. The ravel terminology was first proposed in 2008, with individual ravel types (including, for example, universal 4-ravels) being predicted as possible exotic entanglement modes for both finite and infinite molecular systems\(^1\). The present 20-component, \([\text{Fe}_4\text{L}_{12}]\) ravel entanglement corresponds to a ‘branched knot’ topology, with individual molecules displaying chirality. The unique self-interpenetrating molecular arrangement is stabilized by a favourable combination of \(\pi\)–\(\pi\) interactions and Nature’s tendency to minimize voids in molecular architectures.

**Results**

**Ligand synthesis.** The ligand, 1,1’-(oxybis(1,4-phenylene))bis-4,4-dimethylpentanc-1,3,-dione (LH\(_1\)), was synthesized in 81% yield by a Claisen condensation reaction. The peak at 16.05 p.p.m. in \(\text{H}^1\) nuclear magnetic resonance (NMR) spectrum indicates the ligand exists exclusively in its bis-enol form in chloroform solution.

Triple helicate \([\text{dichloromethaneCFe}_3\text{L}_1]\) and universal 3-ravel \([\text{Fe}_4\text{L}_{12}]\). In an initial experiment, the reaction of LH\(_1\) with ferric chloride in tetrahydrofuran (THF) in the presence of base yielded a deep-red solution that was taken to dryness and the red product recrystallized from a dichloromethane/ethanol mixture. The resulting soluble needle-like crystals (isolated in 88% yield) were used for an X-ray structure determination and shown to be a triple helicate of type \([\text{Fe}_4\text{L}_1]\) (Fig. 1d). The structure revealed that the helicate encapsulates a dichloromethane molecule in its central cavity; this guest is readily lost in a vacuum. Single crystals contain equal amounts of the P and M helical forms.

If instead, diethyl ether vapour was very slowly diffused into the deep-red solution and the resulting mixture allowed to stand for \(~3\) months in a sealed flask, deep-red block-like crystals were obtained. Microanalysis of the vacuum dried crystals showed them...
to have an identical empirical composition to that of the above triple helicate product, but both the crystal habit and the solubility differed (unlike the triple helicate, the latter crystals were insoluble in common laboratory solvents). The yield was near quantitative at 97%. An X-ray structure determination showed that the latter product was an iron(III) cluster of type [Fe₈L₁₈] whose structure (Fig. 1e–g) was characterized by an extraordinary 'self-interpenetrating' arrangement whose connectivity ascribes the universal 3-ravel motif. Comparison of the habits of the bulk crystalline products from the helicate and 3-ravel preparations, as well as comparison of their respective powder X-ray diffraction (PXRD) patterns (which also corresponded to those calculated from the respective corresponding single-crystal X-ray data, Fig. 2), confirmed the homogeneity of each product and that the crystal structures are truly representative of the bulk materials.

Discussion

The unique $D₃$-symmetric universal 3-ravel is derived from 20 individual components (12 ligands and 8 metal ions) and very likely represents the thermodynamic product from the reaction of these components given the extended time required for this interwoven topology to form. Each molecule of the ravel is associated with a helical twist, with all eight iron atoms adopting the same chiral configuration; hence, single molecules are chiral, whereas individual crystals are racemic, containing equal numbers of opposite chiral forms.

Interpenetration of porous polymeric structures is common in the crystalline state, with the driving force usually attributed to the achievement of less void volume in the crystal—in keeping with Aristotle's maxim that 'Nature abhors a vacuum.' In this context, examples of slow interpenetration (and linking) of molecular cages by reversible metal coordination bond formation have been documented previously and, for example, Fujita et al. have pointed out that interlocked cage structures can be more stable than their separated monomer units. Quite recently, interpenetration by slow reversible covalent (imine) bond formation has also been shown to give rise to an organic interlocked cage structure. Although non-covalent interactions such as π–π stacking undoubtedly contribute to stabilization of this product in the solid state, it has been suggested that the generation of a more compact, interpenetrated assembly provides an additional driving force for the formation of the interlocked product in this case.

The operation of a related interpenetration mechanism seems to be a reasonable rationale for promoting the intertwining found in the present [Fe₈L₁₈] assembly. The adoption of the universal 3-ravel topology clearly provides an efficient means of 'space filling' to produce what, overall, is a quite compact molecular arrangement (Fig. 3a). In addition, in the solid state, there is evidence for favourable π–π stacking between aryl rings and these interactions presumably act in concert with the above mechanism to direct the ravel

Figure 2 | The powder X-ray diffraction study. (a) X-ray powder diffraction pattern of [DCMFe₈L₁₈]. The black crosses show the collected data, the red line the calculated Le Bail fit, the green line the difference plot and the vertical blue lines the reflection markers. Modelled using space group no. 61, $Pbca$, $a = 21.625\,(2)$, $b = 19.443\,(1)$, $c = 41.085\,(4)\,\text{Å}$. $R_p = 1.601\%$, $R_w = 2.416\%$, $\chi^2 = 3.252\%$. (b) Powder X-ray diffraction pattern of [Fe₈L₁₈]·15Et$_2$O. The black crosses show the collected data, the red line the calculated Le Bail fit, the green line the difference plot and the vertical blue lines the reflection markers. Modelled using space group no. 163, $P3_1\,c$, $a = 31.968\,(5)$, $c = 24.079\,(4)\,\text{Å}$. $R_p = 1.644\%$, $R_w = 2.578\%$, $\chi^2 = 36.705\%$.

Figure 3 | The universal 3-ravel structure. (a) Semi-transparent space-filling representation of the X-ray structure of the universal 3-ravel, [Fe₈L₁₈] showing the ‘close packing’ of the ravel strands. (b) Schematic representation of part of the crystal structure, [Fe₈L₁₈] showing the top of one of the one-dimensional channels present in the crystal structure; solvate molecules have been omitted for clarity.
assembly process and stabilize the final product; related π-π stacking is absent in the isomeric [Fe3L6] helicate structure shown in Figure 2. A view of the crystal packing is given in Figure 3b.

In this report, we describe the realization of a new class of interwoven molecular nanostructures based on a universal 3-ravel motif. The resulting tightly organized iron(III) nanocluster spontaneously assembles over time from 8 iron and 12 bis-δ-ketonato ligand components. The formation of this unique self-interpenetrating molecular arrangement appears, at least in part, to be driven by Nature’s tendency to minimize voids in molecular architectures. Finally, it is noted that the present ravel structure exhibits both remarkable intricacy and unusual beauty in its molecular form, it thus provides a new member of the small family of diverse interwoven molecular architectures displaying similar attributes reported previously.

Methods

Physical measurements. 1H- and 13C-NMR spectra were recorded on a Bruker 300 MHz spectrometer (Bruker) at 300 K. The electron spray mass spectra were obtained with a Bruker Daltonics Apex Ultra 7T FTICR mass spectrometer (Bruker) with an electrospray ionization source. Elemental analyses for C, H and N were performed by Campbell Microanalytical Laboratory, University of Otago. Infrared spectra were recorded on a Varian 800 Fourier transform infrared spectrometer (Varian) as KBr pellets.

Preparation of LH3. 3,3-Dimethyl-2-butanone (2.1 g, 21.0 mmol) in THF (100 mL) was added dropwise to a stirred suspension of NaH (2.5 g, 63.0 mmol, 60% oil dispersion) in THF (150 mL) under nitrogen at room temperature. After 10 min the resulting mixture was treated with a solution of 8-oxazine-bis(methylene benzolate) (3.0 g, 10.5 mmol) in THF (100 mL), which was added dropwise over 20 min. The mixture was heated at reflux overnight during which time it slowly turned yellow. The solution was allowed to cool and the solvent was removed. The yellow residue was dissolved in ice water (200 mL), the solution was filtered and diethyl ether (60 mL) was added to the filtrate and the mixture was shaken. The aqueous phase was separated, then acidified with dilute hydrochloric acid to yield a precipitate. This mixture was allowed to stand for 1 h in an ice bath and the precipitate was collected by filtration and recrystallized from an acetone/ethanol mixture to yield colourless crystals. Preparation of LH4. In a 100 mL round-bottom flask, 8-oxazine (1.0 g, 0.012 mol) in dry THF (10 mL). The mixture was stirred for 1 h before anhydrous iron(III) chloride (26 mg, 0.16 mmol) dissolved in THF (40 mL) was added dropwise. The mixture was stirred overnight, during which time the colour changed to deep-red. The mixture was filtered and the filtrate was collected. The solvent was removed on a rotary evaporator and the crude solid obtained was recrystallized from DCM/ethanol (Vv = 1:1). Yield 97% (80%). A red needle from the solution was used directly for the X-ray structure determination. Analysis (calcd, found for C31H40FeO3, C: 73.79, 73.83, H: 7.17, 7.39).

Preparation of [Fe3L6]Cl2. LH3 (100 mg, 0.24 mmol) in dry THF (40 mL) was added dropwise to NaHCO3 (1.1 g, 0.012 mol) in dry THF (10 mL). The mixture was stirred for 1 h before anhydrous iron(III) chloride (26 mg, 0.16 mmol) dissolved in dry THF (40 mL) was added dropwise. The mixture was stirred overnight, during which time the colour changed to deep-red. The mixture was filtered and the filtrate was collected. The solvent was removed on a rotary evaporator and the crude solid obtained was recrystallized from DCM/ethanol (Vv = 1:1). Yield 97% (80%). A red needle from the solution was used directly for the X-ray structure determination. Analysis (calcd, found for C31H40FeO3, C: 73.79, 73.83, H: 7.17, 7.39).

Single-crystal X-ray diffraction measurements. X-ray structural data were collected on a Bruker-Nikon APEX2-X8-FRS91 diffractometer (Bruker-Nikon) using graphite-monochromated MoKα radiation generated from a rotating anode (0.71073 Å) with an anode current at 150 kV (ref. 23). Multiscan empirical absorption corrections were applied using the programme SADABS.26 Data integration and re- 

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Author contributions
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