



# Molecular weaving

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**Historically, the interlacing of strands at the molecular level has mainly been limited to coordination polymers and DNA. Despite being proposed on a number of occasions, the direct, bottom-up assembly of molecular building blocks into woven organic polymers remained an aspirational, but elusive, target for several decades. However, recent successes in two-dimensional and three-dimensional molecular-level weaving now offer new opportunities and research directions at the interface of polymer science and molecular nanotechnology. This Perspective provides an overview of the features and potential of the periodic nanoscale weaving of polymer chains, distinguishing it from randomly entangled polymer networks and rigid crystalline frameworks. We review the background and experimental progress so far, and conclude by considering the potential of molecular weaving and outline some of the current and future challenges in this emerging field.**

The word ‘complexity’ stems from the Latin ‘plectere’, which means to entwine or weave. Indeed, weaving remains one of the most enduring and effective means to create complex, ordered materials whose properties differ fundamentally from those of the unorganized components. The weaving of one-dimensional (1D) strands, which range from threads with diameters measured in millimetres (reeds, plant fibres and so on) to those of a few micrometres (wool, cotton, synthetic polymers, spider webs and so on), into 2D fabrics has underpinned technological advances through the ages<sup>1</sup>. In contrast, the construction of woven nanoscale structures is in its infancy. Molecular weaving is the regular entanglement of 1D, ideally flexible, molecular strands into an extended 2D fabric or 3D network. As with macroscopic yarns, a molecularly woven material should have long-range order in each dimension of the weave, with the strands mechanically associated through periodic orderly entanglements. In a similar manner to conventional textiles, molecular weaving can induce characteristics and properties substantially different to those of the unwoven constituent polymer strands. However, there are also fundamental differences in weaving fibres at different length scales: in macroscopic weaves, friction and inertia maintain the position of entangled strands; at the molecular level, random thermal motion leads to substantial reptation of the strands above the glass transition temperature, which could cause fraying and some dethreading unless there are interactions (for example, hydrogen bonding,  $\pi$  stacking, metal coordination, anion binding and so on) that stabilize the arrangement of adjacent or entwined strands.

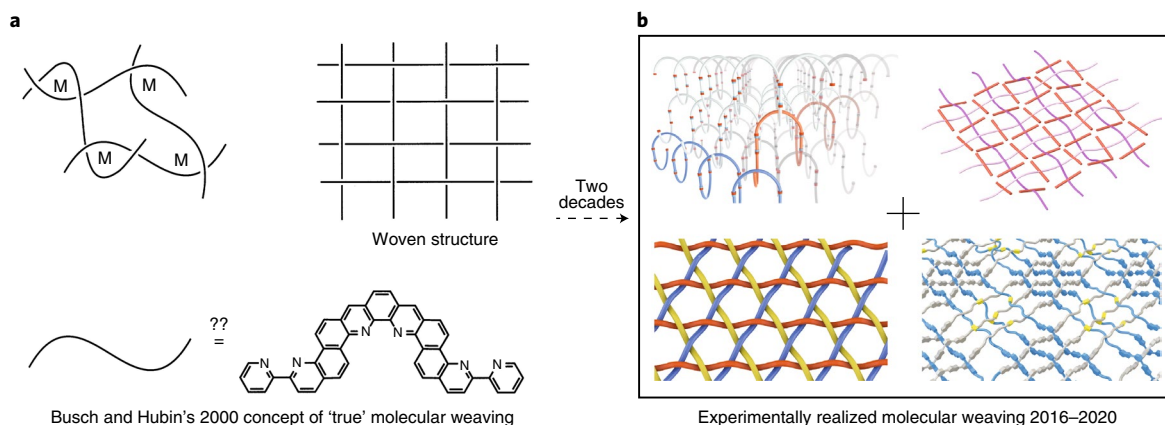
The synthesis of molecularly woven polymers has been targeted for some considerable time. In 1992, less than a decade after Sauvage’s seminal metal template synthesis of a [2]catenane<sup>2</sup>, Busch (who was among the first<sup>3</sup> to recognize and exploit metal template effects in chemical synthesis) predicted<sup>4</sup> the possibility of ‘molecular weaving’ from ‘orderly entanglements’ based on metal coordination complexes. A few years later, Busch and then-graduate-student Hubin proposed<sup>5</sup> a vision for interlaced molecular designs that included the concept of ‘true’ molecular weaving, shown in Fig. 1. Busch and Hubin suggested that “The ultimate aspiration of chemists working on interlocked structures might be to weave molecules as if they were macroscopic threads,” and concluded that “Although this goal seems distant, progress is being made.”<sup>5</sup> They also stressed that “the use of the word ‘weaving’ should be reserved for

covalently linked molecular strands mechanically interlocked by multiple crossovers (interfacings) with multiples of other strands” and that “‘Weaving’ should not be used to describe solid state structures where hydrogen bonds or other weak interactions mimic truly covalently interlocked motifs.”<sup>5</sup>

As such interlaced molecular structures start to become synthetically accessible, it is timely to revisit the Busch–Hubin suggestion for what should be considered molecular weaving. Their rationale for requiring continuous covalently linked polymer backbones was doubtless because dynamic or weak bonding (for example, labile metal–ligand coordination bonds or hydrogen bonds) would eliminate the mechanical restriction on strands that pass through each other<sup>6</sup>. This is the crucial feature that imparts woven structures, at any length scale, with distinct and particular properties (and also what connects the mathematics of weaving to knots, that is, topology)<sup>7</sup>. However, at the molecular level, reversible (dynamically labile) covalent bonding could also permit polymer strands to pass through each other, whereas non-covalent (supramolecular) interactions might be sufficiently robust to restrict strand passage under some conditions.

As with mechanically interlocked molecules (catenanes, rotaxanes and knots)<sup>8,9</sup>, thermodynamic stability and template synthesis is likely to prove useful to assemble woven molecular materials, but the kinetic stability of individual strands is a crucial part of maintaining the weaving pattern and imparting the particular characteristics associated with weaving. In addition, strands should remain associated in the material’s pattern by virtue of the weave, not require being attached together at fixed points (for example, by covalent bonds or metal ion coordination—residual or intended—or other strong non-covalent interactions) to prevent unravelling. Nevertheless, interstrand interactions are likely to be helpful in stabilizing a weave, and perhaps in the future might be used to change the shape or structure of the strands within the weave in response to stimuli. Furthermore, both the contact and space fields (Box 1) of molecular weaves have the potential to accommodate ligand sites and other chemical functionality, which brings into play properties such as molecular recognition, absorption, gas storage and catalysis using the weave. Accordingly, while recognizing the importance of kinetic stability for any woven structure, instead of being too prescriptive about the types of bonding involved in a particular structure, it may be better to simply focus on whether properties

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**Fig. 1 | Busch and Hubin's concept of 'true' molecular weaving and recent experimental examples of molecularly woven structures.** **a**, Grids of interwoven strands, assembled using metal ion templates, envisioned by Busch and Hubin<sup>5</sup> to be used to construct materials made of woven polymer strands. Panel **a** reproduced with permission from ref. <sup>5</sup>, Elsevier. **b**, Weaving patterns of experimentally realized 3D woven COFs<sup>39</sup>, and 2D woven supramolecular<sup>83</sup> and molecular<sup>38,86</sup> materials.

are usefully induced and affected by the periodic interlacing of the components at the nanoscale.

Expanding on their initial metal–template synthesis of a [2]catenane, in the 1980s and 1990s Sauvage's group used linear metal helicates to prepare molecular trefoil knots and Solomon links<sup>9</sup>. This (three and four crossings, respectively) is probably the effective limit of knots and links that can be achieved through a linear helicate approach because of the intrinsic difficulty in distinguishing strand ends that need to be joined over long distances to generate closed-loop structures<sup>10</sup>. However, weaving does not have the same requirement and it can be envisaged that linear double (and potentially triple and quadruple<sup>11</sup>) helices may find utility as building blocks for molecular weaving. Moreover, major advances in molecular nanotopology have been made using other strategies to prepare knots and links over the past decade<sup>12–18</sup>. In particular, circular helicate<sup>19–21</sup>, braiding<sup>22</sup>, chaperone<sup>23</sup> and other<sup>18,24</sup> approaches have been used to control the number, stereochemistry and sequence of crossings to make well-defined molecular tangles, together with methods developed to combine them to form progressively more complex synthetic molecular knots and links.

In our everyday world, the deliberate action of knotting is closely related to both knitting and weaving. Knotting usually refers to an entanglement within a single 1D strand (mathematically a line or 1D manifold) or, colloquially, to the random entanglement of multiple strands. Knitting is the entanglement of a single 1D strand in a particular pattern (generally regions of periodic ordered tangles) that results in a layer (mathematically, a surface or 2D manifold) that may adopt a complex 3D curvature (such as a knitted hat or sweater). Weaving is the regular mutual entanglement of multiple strands in 2D or, sometimes, 3D. All three processes require the formation of orderly strand entanglements. Therefore, it seems reasonable that insights from molecular-scale knotting might be used to inform approaches to other types of material based on molecular entanglement.

### Synthetic methodology for the assembly of orderly entanglements in molecular knots and links

In view of the similarity of knotting and weaving, the methodology and design strategies developed to prepare orderly molecular entanglements<sup>25</sup> in the form of synthetic molecular knots<sup>26–33</sup> and links<sup>34–36</sup> should be generally transferable to molecular weaving (and, in due course, to a molecular equivalent of knitting(!)). The intricate structural considerations often involved in successful molecular knot<sup>12</sup> and link<sup>37</sup> syntheses is illustrated by the examples shown in Fig. 2.

For the  $5_1$  pentafoil knot<sup>19</sup> (Fig. 2a), Star of David link<sup>20</sup> (Fig. 2b) and  $8_{19}$  knot<sup>22</sup> (Fig. 2c), metal template helicate formation is used to create multiple crossings of the same handedness. The  $-\text{CH}_2\text{CH}_2-$  spacer between the bipyridine chelate groups thermodynamically favours the formation of cyclic pentameric or hexameric over that of linear helicates (which are often the initially formed kinetic products), whereas the  $-\text{CH}_2\text{OCH}_2-$  spacer directs the assembly of a tetrameric circular helicate. The anion template determines the size of circular helicate ( $\text{Cl}^-$  = tetrameric or pentameric) and therefore the number of inner crossings (four or five). Reversible imine bond formation allows the correction of high-energy structures, formed by incorrect strand connections, to give the desired low-energy structure. The presence of the oxygen atoms in the  $-\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}-$  unit provides a stereoelectronic gauche effect and reduces 1,4-CH steric clashes; both effects thermodynamically favour a conformation that connects the strand crossing points in the required (over–under)<sub>5</sub> sequence to bring about the connection of crossings with the necessary pattern and relative stereochemistry for a  $5_1$  knot.

Many of these design elements are also present in the Star of David link<sup>20</sup> (Fig. 2b), but now the absence of a  $\text{Cl}^-$  template favours a hexameric circular helicate. In this system, the formation of the necessary connections between crossings is directed by introducing a biphenyl motif to restrict the conformational space available to the open-chain precursors. Ring-closing olefin metathesis joins the chain ends in robust  $\text{C}=\text{C}$  bonds, which allows the metal (and anion) templates to subsequently be removed to leave a wholly organic entangled molecular structure. The direction and extension of the crossing-point connector for the  $8_{19}$  knot provides a non-alternating crossing sequence, (over–over–under–under)<sub>4</sub>, rather than the alternating (over–under)<sub>n</sub> crossing sequence generated in the other two knots and links.

Many of the design principles established to control the sequence and stereochemistry of periodic entanglements in molecular knots and links should be generally applicable to molecular weaving of extended arrays in 2D and 3D. To do so, intermolecular connections need to be favoured over intramolecular closures with sufficient control to achieve an effective material uniformity. Methods to achieve this thus far involve either (1) connecting preformed tangles using orthogonal chemistry<sup>38</sup> or (2) the use of rigid building blocks and crystal engineering (reticular chemistry)<sup>39–41</sup> to establish intermolecular connections and relative stereochemistry of strand crossings.

**Box 1 | Macroscopic versus molecular weaving, and periodic versus random entanglements**

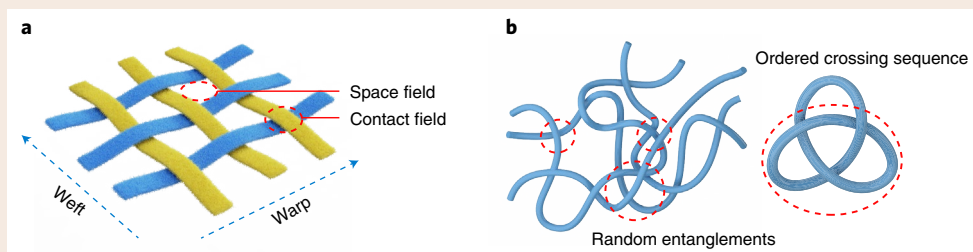
Macroscopic weaving already has a well-established lexicon to describe the interlacing of different strands. In most cases, this terminology can be directly applied to molecularly woven fabrics.

Traditional weaving involves the interlacing of ‘warp’ and ‘weft’ strands, oriented at specific angles to one another (panel **a**)<sup>1</sup>. Textiles are normally woven from top to bottom using complete strands, with one end of each weft strand pulled back and forth (that is, over or under) through the warp strands. In contrast, the weaving of molecular structures does not need to begin from the preformed full-length strands. Chemical strategies have focused on producing some or all of the weaving pattern from single crossings or preformed tangles and extrapolating those crossings (or crossing patterns) through covalent bond formation in 2D or 3D to form a periodic structure with long-range order.

In conventional woven fabrics, warp strands run vertically to the yardage of the material, corresponding to up and down in a loom; weft threads run back and forth through the warp threads and side to side in a loom. In anisotropic molecularly woven fabrics (where the crossing pattern differs in each direction), we suggest that the warp strands are defined as those with the least over–under transitions per unit length.

There are two main parameters used to describe the mechanical properties of conventional woven fabrics. ‘Firmness’ is a measure of how tight and strong the fabric is, whereas ‘flexibility’ is the ability of the material to be deformed. These properties are principally influenced by the strength of the individual fibres, the amount of space between the interlaced strands (the ‘space field’, panel **a**) and the weaving pattern. ‘Stiffness’ (force required per unit displacement) and ‘elasticity’ (the relationship of stress to strain and Young’s modulus) are two parameters related to mechanical properties that in, molecularly woven structures, are likely to be influenced by the chemical constitution of the strands, the non-covalent interactions between the strands and the weaving pattern. The weaving pattern affects the properties of macroscopic woven materials by regulating the interstrand contacts and the space field (panel **a**) and the way that the material responds to stress and strain.

Entanglements in polymer chains prevent strands being able to move freely (panel **b**). Ordered entanglements in the form of periodic sequences of over and under crossings occur in knots, links and weaves. Random entanglements occur in any polymer chains of sufficient length and flexibility<sup>91</sup>.

**Modelling molecular-level entanglement**

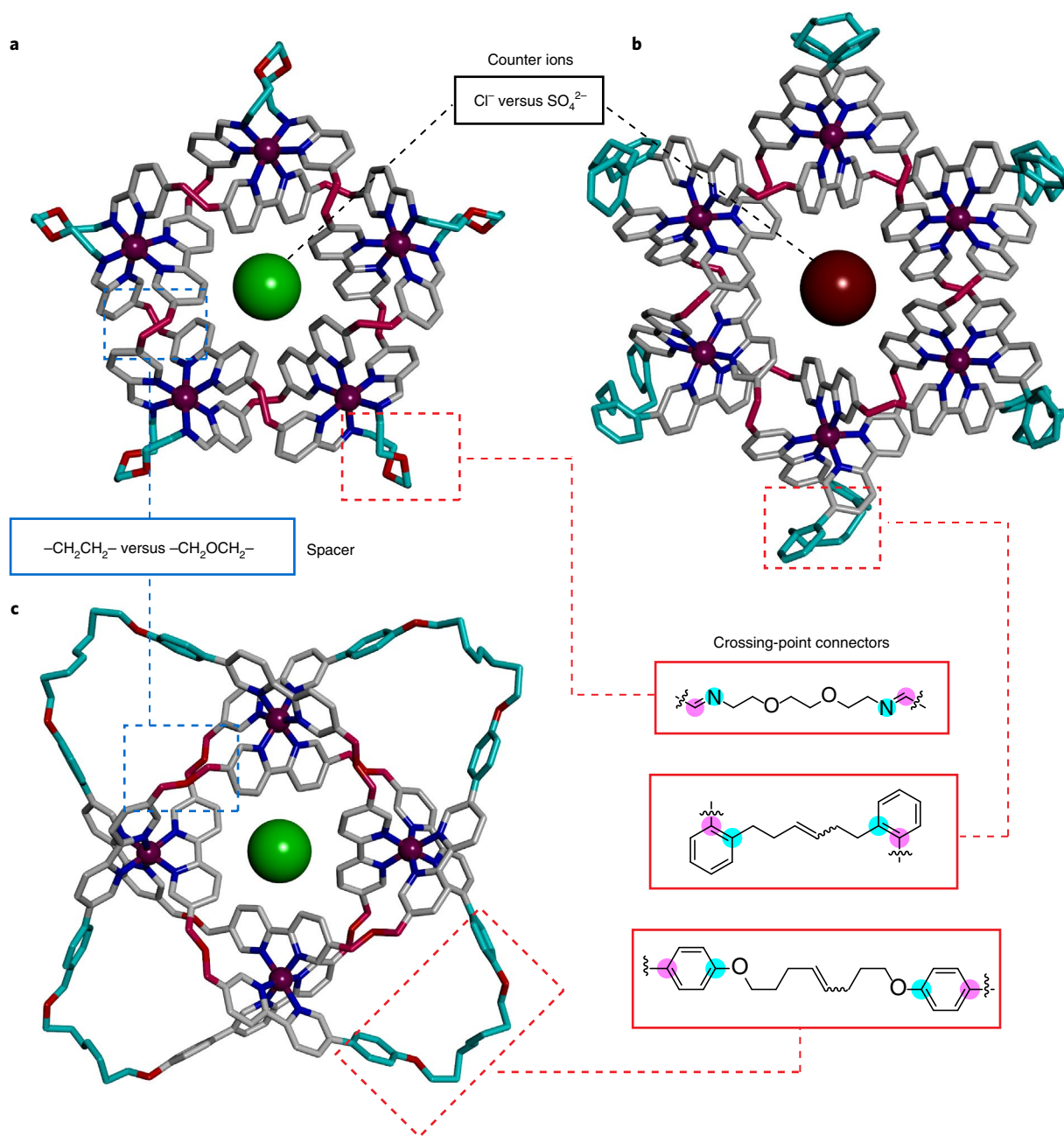
Knots, knits, weaves and randomly entangled networks are different types of mechanically restricted systems. A range of different frameworks are used to model random entanglements in polymer systems (Fig. 3). Here we consider which aspects of these approaches are best placed to potentially bridge the gap between random entanglements and orderly entangled polymer chains and be most useful for predicting the properties of molecular weaves and fabrics.

The behaviour of randomly entangled networks is predicted by theories and models that describe the influence of molecular-level entanglements on the mechanical and dynamic properties of materials. Various descriptions include the tube model<sup>42–44</sup>, slip-link model<sup>45–47</sup>, slip-spring model<sup>48–50</sup> and topological theory<sup>51,52</sup>. Molecular simulations based on each of these approaches aid the understanding of molecular entanglements<sup>53–57</sup>. Early theories<sup>58</sup> of polymer rheology regarded entanglements as transient, physical crosslinks created and broken incessantly by random molecular motion. In tube models (Fig. 3a), the motion of the polymer chain is constrained within a tube-like volume with restrictions that arise from entangled areas being regarded as fixed obstacles<sup>42–44</sup>. Various tube-based models<sup>59–62</sup> have been successfully used to determine the contribution of entanglements to the elasticity of entangled networks for a range of polymers<sup>63</sup>, but generally fail to predict the behaviour of polydispersed systems<sup>48</sup>.

In comparison, the slip-link model (Fig. 3b) successfully predicts the rheological behaviour of many entangled polymer networks by modelling the entanglement junctions as links through which the polymer chain is allowed to slip freely<sup>45–48</sup>. In the related slip-spring model (Fig. 3c)<sup>49,50</sup>, entanglements are considered as additional

slip-springs (grey springs in Fig. 3c), which mimic the dynamics of entanglements with fluctuations of the slip-link points. This model has proved successful in predicting the linear viscoelastic data of monodispersed polymer melts. The slip-link and slip-spring models have also been modified to accommodate various second-order effects<sup>64,65</sup>. Although these models were developed to simulate random entanglements, they appear to provide a suitable basis for investigating the properties of periodically ordered entanglements.

An alternative way to model molecular weaving is to apply topological theory by considering weaving as the sum of connected tangles<sup>12</sup>. The mechanical constraints within an entangled polymer network are similar to the topological restrictions within the tangles of knotted closed loops (Fig. 3d). Studies on the mechanical and dynamic properties of knotted polymers and DNA, both experimentally<sup>66</sup> and by simulation<sup>54–57</sup>, show that the degree and type of knotting in such systems affects their properties. Although it has not led to a systematic theory of modelling entanglements, this approach has provided fresh insights into mechanistic studies on entangled polymers<sup>51,52</sup>. Unlike random entanglements that lack long-range order, molecularly woven fabrics that consist of entanglements with a regular under–over repeat sequence are effectively an infinite periodic extension of the tangles in particular knots and links. For example, the simplest 2D weaving pattern, the plain weave, is a continuous repeating polymer formed from the precursor, in this experimentally realized case an interwoven 3 × 3 grid<sup>33</sup> used to construct a 7<sub>4</sub> knot (Fig. 3e), although potentially any size of  $n \times n$  grid could prove suitable. This suggests that topology and tangle theory could also be usefully applied to model the properties of regular molecularly woven materials.



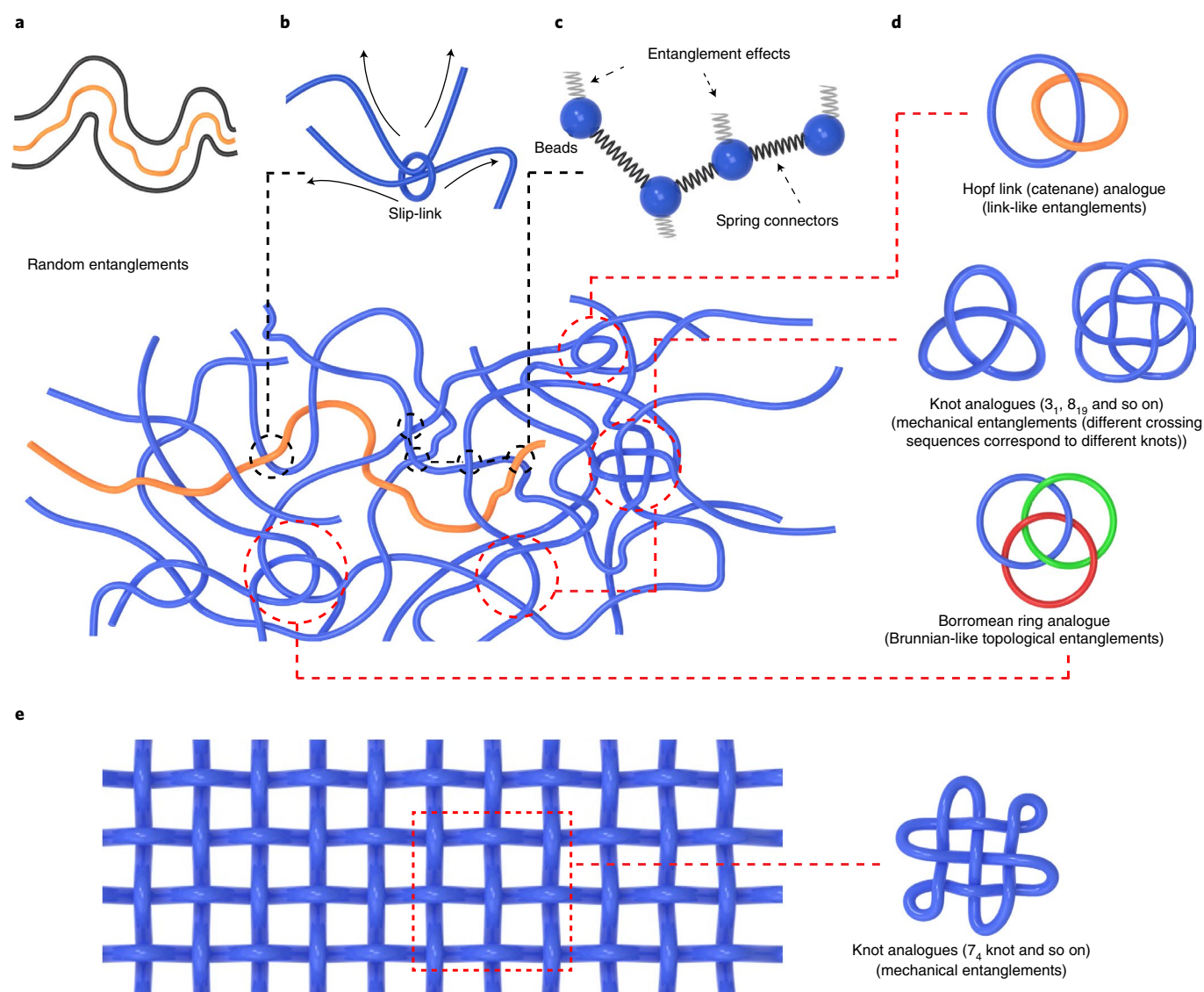
**Fig. 2 | Methodology for controlling crossing stereochemistry and connectivity.** **a–c.** Examples of the ways that the geometry, crossing points and connectivity of ligand strands are controlled in the synthesis of molecular knots (**a,c**)<sup>19,22</sup> and links (**b**)<sup>20</sup>. Similar strategies are likely to be useful for controlling periodic entanglements for molecular weaving.

Given the significance and widespread occurrence of random, or at least non-periodic, entanglements in DNA and other polymers, and the scarcity of experimental examples of periodic molecularly woven systems, the simulation of entanglement–property relationships has focused on randomly entangled polymer networks and systems with short-range order. The questions of how long-range order in molecularly woven materials can affect the mechanical and dynamic properties, and how the properties of periodic orderly entanglements of flexible chains<sup>38</sup> differ to those of randomly entangled polymer networks<sup>66</sup> and rigid-strand covalent organic framework (COFs)<sup>39</sup>, remain open. Understanding how the regularity and complexity of entanglements can affect polymer properties is a key challenge for the design of molecularly woven materials.

### Experimental realization of molecular weaving

Until recently, synthetic nanoscale weaves featuring regular periodic entanglements in 2D or 3D remained limited<sup>67,68</sup> to DNA<sup>69</sup> and coordination polymers<sup>70–78</sup> that featured either dynamically labile metal–ligand bonds in the backbone or strands chemically connected together at fixed points. However, in the past few years, a number of different experimental strategies<sup>79,80</sup> have been developed to form molecularly woven organic polymers.

In 2016, Yaghi and co-workers generated a 3D COF with periodic entanglements of rigid helical organic polymer strands through the use of reticular chemistry to telescope unoriented crossings based on a Cu(I) bis(phenanthroline) complex (Fig. 4a)<sup>39</sup>. The resulting 3D woven COF, COF-505, has helical strands interlaced at

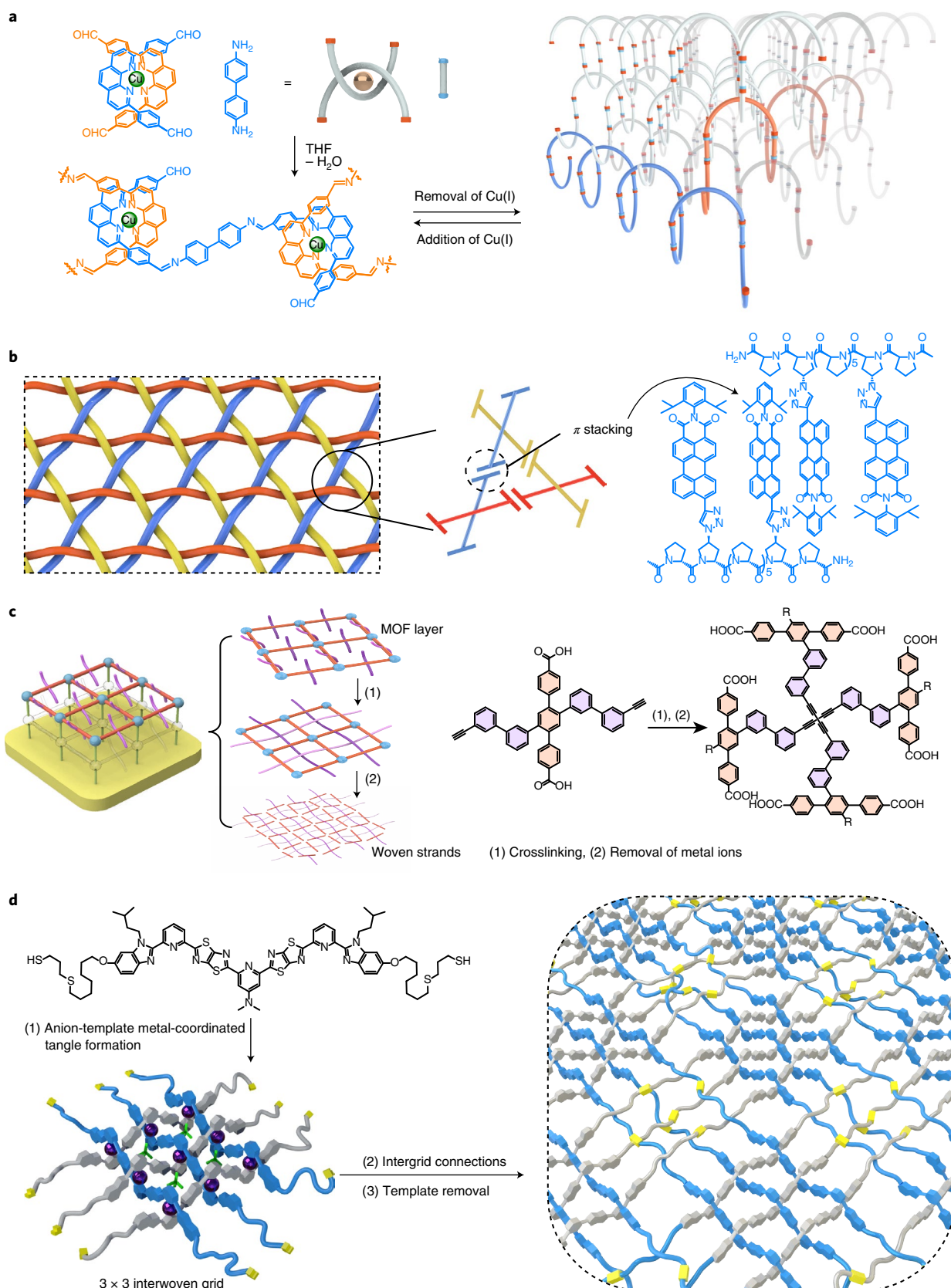


**Fig. 3 | Overview of frameworks used to model random molecular-level entanglements.** **a**, The tube model constrains the dynamics of polymer chains within a tube-like region in which the chains can slide around but not through each other (termed ‘reptation’ or ‘creep’)<sup>42–44</sup>. **b**, Slip-link model, in which the effects of entanglements are represented by slip-links with the polymer chains free to slide through the junctions<sup>45–47</sup>. **c**, Slip-spring model, which considers entanglements as slip-springs (shown in grey), which mimic the chain dynamic properties by incorporating fluctuations of entanglements based on a Rouse chain (in which the polymer chain is divided into  $N + 1$  beads connected by  $N$  springs, which experience friction that arises from the fast collisions with neighbouring chains, shown by black dashed circles)<sup>48</sup>. **d**, The tangles present in molecular knots and links can provide a topological model for multi-entangled polymer chains<sup>52</sup>. The Hopf link (simple [2]catenane) mimics link-like entanglements in which two or more strands are mechanically entwined. Mechanical entanglements generated by knotting a single strand in different crossing sequences can be related to closed-loop knots, such as the  $3_1$ , which has an alternating crossing sequence (over-under-over-under), and  $8_9$ , which has a non-alternating crossing sequence (over-over-under-under). Strands that are prohibited by topology from crossing over and under another strand are related to Brunnian topologies, such as Borromean rings. **e**, The simplest 2D woven fabric (box or plain weave), which features periodic entanglements, consists only of mechanical entanglements formed by repeating the interwoven  $3 \times 3$  grid<sup>33</sup> used to construct a  $7_4$  knot. Note that the stereochemistry of a box weave requires horizontally or vertically adjacent  $n \times n$  grids to be mirror images.

regular intervals in 3D, and the Cu(I) ions serve as points of registry. After the removal of 92–97% of the Cu(I) ions, the resulting material showed an increased elasticity compared with that of the original COF despite the strands still being crosslinked by metal ions every  $\sim 20$  binding sites, on average, sufficient to prevent substantial strand reptation. Related woven COFs were shown to have a guest-adaptive property attributed to the limited movement of the rigid strands, still crosslinked by residual metal ions, within the framework<sup>40,41</sup>. Using a similar strategy, Loh and co-workers constructed several crosslinked COFs using Cu(I) (ref. <sup>81</sup>) and Ag(I)

(ref. <sup>82</sup>) 1D molecular organic frameworks (MOFs) followed by a postmodification connection of the strands, although there is not yet evidence to suggest that the crosslinked strands are entangled in the form of a regular periodic weave.

In 2017, the Wennemers group reported an extended triaxial supramolecular kagome weave that consisted of oligoproline segments with  $\pi$ - $\pi$  stacking between pendent perylene monoimide units that connected the molecules to form a periodically entangled array (Fig. 4b)<sup>83</sup>. The non-covalent connections mean that the strands can, in principle, pass through each other without being



**Fig. 4 | Examples of strategies to synthesize molecularly woven materials.** Types of organic material prepared so far with periodic nanoscale entanglements. **a**, A 3D interwoven COF formed from a Cu(I) complex of a single crossing point using a reticular approach that results in a strand crossing pattern<sup>39</sup>. **b**, A supramolecular kagome weave held together using non-covalent interactions (aromatic stacking between rotated perylene-monoimide units at the end of each strand)<sup>33</sup>. **c**, A surface-supported layered MOF in which crosslinking is formed via Glaser-Hay couplings<sup>36</sup>. **d**, A 2D molecularly woven fabric formed via tessellation of a 3 × 3 grid. Interwoven 3 × 3 grids<sup>33</sup> can be connected intermolecularly in layers to generate the required crossing pattern for a molecular weave. Subsequent removal of the metal ion templates affords the wholly organic molecularly woven fabric<sup>38</sup>.

mechanically restricted. Other supramolecular materials have been prepared with woven scaffolds that have dynamic hydrogen bonds at crossing points, which similarly intrinsically rules out effects being induced by strand entanglement<sup>84,85</sup>. However, it may prove possible to modify such systems so that the crossing pattern can be covalently captured to achieve a molecularly woven material of organic polymer strands.

The Mayor group prepared a 2D woven polymer network using a MOF template approach, in which the linear weft and warp threads were preorganized by Cu(I) on a surface-mounted MOF and a woven structure subsequently formed by Glaser–Hay couplings (Fig. 4c)<sup>86</sup>. Unfortunately, the weave is not sufficiently robust to be self-sustaining and the woven network disassembles to give the individual polymer strands on removal of the metal ion templates.

In 2020, our group generated the periodic entanglements of a weave through the 2D tessellation of prewoven tangles (Fig. 4d)<sup>38</sup>. A woven 3 × 3 grid<sup>33</sup> that crystallizes in off-set layers was polymerized in 2D using disulfide bond formation, a chemistry compatible with the formation of a woven building block. On removal of the ion templates, the resulting wholly organic molecularly woven fabric is effectively the realization of the structure shown in Fig. 1 proposed<sup>4,5</sup> by Busch and Hubin three decades earlier. There are undoubtedly defects in the pattern of the experimentally produced weave, in part caused by a lack of control over which of the three strand termini of a grid edge connect to which of their counterparts along the edge of the adjacent tessellated grid. Other issues, such as the relative stereochemistry of connecting grids, also affect the crossing sequence produced when strands from preformed tangles are joined together.

Despite these deficiencies, preliminary indications of the effects of molecular weaving could be assessed by comparing the properties of the material that consists of layers of molecularly woven polymer chains with those of the component, but unweaved, 1D polymer. Unlike the unweaved polymer, when the molecularly woven fabric was deposited on a polyester substrate that could be stretched, the material was found to tear along ordered, geometric lines, as for a macroscopic fabric with the same weave pattern, and to delaminate as the woven layers slid over each other. The molecularly woven fabric was almost twice as strong as the unweaved strands of the same chemical composition<sup>38</sup>.

These mechanical properties of the material can probably be attributed to the physical restriction on the strand movement imposed by the contact field (Box 1) and weave pattern. However, the space field (Box 1) of the molecular weave could also be exploited. When incorporated into a polymer-supported membrane, the 2D molecularly woven polymer acts as a net, which slows the passage of ions larger than 2 nm, whereas they pass through membranes that incorporate the unweaved polymer strands much more rapidly. For ions smaller than 2 nm, the rate of diffusion through the membrane is similar for both the woven and unweaved polymers<sup>38</sup>.

### Challenges and potential

The ability to weave molecular chains in periodic orderly entanglements—to form molecularly woven materials<sup>5,67,68</sup>—marks the intersection<sup>87</sup> of polymer science<sup>88</sup> and molecular nanotopology<sup>15</sup>. With molecularly woven materials now becoming accessible, it is timely to consider some of the immediate, and more long-term, challenges for this nascent field. In addition to the need to invent, optimize and discover the limitations of different methods and strategies for weaving molecular strands, below we proffer a number of open-ended challenges and aspirational goals for molecular-level weaving:

To obtain different weaving patterns, possibly using strands of different compositions, but ultimately obtaining different weaves using the same type of strand.

To determine how different weaving patterns, errors in the weave, strand rigidity and interstrand non-covalent interactions affect the properties.

To understand how the introduction of additional hydrogen bonding,  $\pi$  stacking or electrostatic interactions change woven strand conformations.

To investigate whether molecular switches or motors can be used to actuate strands, shortening or lengthening particular segments to cause a 2D molecularly woven fabric to fold into different programmed shapes.

To find if a 2D molecularly woven fabric can be induced to mould itself around a shape like a macroscopic sheet, perhaps not through the force of gravity, but maybe as a result of non-covalent interactions.

To determine what are the fundamental differences between, and possibilities for, 2D and 3D weaving.

To study how the mesh of the weave can be exploited (size, shape, chemical constitution and appending functional groups).

As an alternative to the self-assembly of small building blocks, to find if it is possible to weave preformed polymer strands in a manner reminiscent of the folding of polymer chains into different knots induced by artificial metal ion ‘chaperones’.

To investigate if such chaperones be used to ‘knit’ a single 1D polymer chain into a persistent 2D layer held in shape by periodic entanglements.

To determine if conventional polymers (polystyrene, poly(methylmethacrylate), polyethylene terephthalate and so on), or something like them, can be woven or knitted.

Several of these challenges warrant further comment. Using different experimental conditions, crystal engineering and reticular chemistry often produce different architectures (polymorphs) from the same or similar building blocks, and so it may not be unreasonable to hope that this may also occur, by chance or design, in molecular weaving (the first challenge laid out above). Furthermore, recent success in the tying of different knots in a molecular strand using metal ions as artificial chaperones<sup>23</sup> for folding and entanglement may provide an approach to form tiles with different tangles from the same building blocks for the ‘tessellation of preformed tangles’ strategy.

The tessellation strategy also allows the combination of different tangles to form different weaving patterns by selecting tangles with the required repeating pattern. Furthermore, by combining multiple different tiles in a controlled manner, through matching chemical connectivity and geometry, complex weaving patterns could be built up. Given the number of known and potentially accessible preformed tangles, and the combinations they could form, the synthetic variations provided by this strategy could be great indeed.

Despite the wealth of potential weaving patterns that could be formed from these strategies, to experimentally determine one from another at the molecular level represents a considerable challenge. Furthermore, they are all likely to develop defects within the molecular weave. These could take the form of missing crossings, swapped strands and loops, and interlayer connections. Investigations into how these errors might affect the properties of woven materials, or how they can be prevented, will be hindered by the challenges in characterizing such materials. Errors in the weave are likely to be disordered across multiple sites, and therefore not easily probed using methods that rely on periodic short-range order, such as X-ray or electron diffraction. Instead, improvements in both the utility and resolution of techniques that probe individual molecules, such as scanning tunnelling microscopy, transmission electron microscopy and atomic force microscopy, may prove useful in this regard.

The weaving of fully formed polymer strands (the eighth challenge laid out above) will be particularly challenging in view of the number of conformations that, in principle, need to be sampled (similar to the classic protein-folding problem) and the kinetic

barriers to entanglement already observed<sup>23,2731</sup> in small-molecule knotting. It may be that this issue can be overcome using artificial chaperones. This challenge, and others, may benefit from incorporating non-covalent interstrand recognition elements into the chains, to assist the formation of particular folded conformations rather than to rely solely on topology to control geometry.

In connection with the folding of long chains, the unfolding or untangling of molecularly woven fabrics has yet to be explored. When prepared through any template strategy, the woven fabric, after template removal, represents a kinetically trapped high-energy state of ordered entanglements. Molecular knots, prepared using a similar template strategy, spontaneously and rapidly unravel when not tethered in a closed loop and the same could be expected of a molecularly woven fabric—albeit over a longer timescale. The disentangling of some systems has been reported<sup>86</sup>, but the kinetics of such a process and how it is linked to polymer length, number of entanglements and the strength of interstrand interactions is currently unknown.

There is clear potential for molecularly woven materials to have enhanced physical and mechanical characteristics (for example, five times stronger than steel weight for weight<sup>89</sup>). Initial results on the artificial 2D molecularly woven fabric shown in Fig. 4d demonstrated<sup>38</sup> substantially improved strength, as well as separation and permeability properties related to the synthetic material having a relatively uniform mesh size. With a view to other potential applications, we note that some porous COFs (albeit unwoven examples thus far) were shown<sup>90</sup> to be able to collect atmospheric water. However, perhaps one of the most intriguing prospects for materials could be the integration of molecular weaving with elements of molecular machinery that can change the length, conformation and/or crossing registry of individual strands within the weave, to cause a 2D molecularly woven fabric to adopt different 3D shapes (challenge 4). Such technologies may seem today like science fiction, but probably no more so than Busch's vision did 30 years ago.

These are just some of the questions, challenges and opportunities posed by the recent invention of molecular-level weaving, a new form of well-defined complexity in the structural organization of matter. The possibilities for which are—of course(!)—as long as a piece of string.

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## Competing interests

The authors declare no competing interests.

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