

of polydispersed inorganic nanoparticles during isotropic agglomeration¹¹. As opposed to extended hierarchical assemblies¹², the growth of nanoparticle clusters stops at the point when the weak attractive interactions that initially drive the aggregation process are counteracted by the gradually increasing electrostatic repulsion as nanoparticles become part of the growing aggregate¹¹.

With regard to sophisticated self-organization processes, and in comparison to proteins, nucleic acids and other biological building blocks, the distinguishing feature of inorganic nanoparticle aggregates assembled by oriented attachment is the ability of the resulting superstructures to delocalize charge carriers. Indeed, the oriented-attachment process eliminates the typical insulating gaps in-between the components of inorganic assemblies and thus leads to an increase in the charge transport — of considerable practical importance in, for example, electronic devices and catalysis¹³. In fact, Banin and collaborators demonstrate that the nanorod couples acquire special optical properties compared with single nanorods as a consequence of charge delocalization over the entire conductive loop. This can be seen from the electron and hole states of the band-edge states. In the case of single nanorods, the wavefunctions of both electrons and holes encompass the entire nanorod, whereas the excited states of the nanorod couples concentrate their carrier density in the end caps. The immediate practical consequences of such a big difference in electronic states can be envisioned for photocatalysis. Barring a considerable shortening of the lifetimes of the excited states — something that remains to be investigated — photoinduced reactions involving both electrons and holes could proceed with greater efficiency in nanorod couples than in single nanorods.

Interestingly, some of the nanorod couples are not planar and show a distinct dihedral

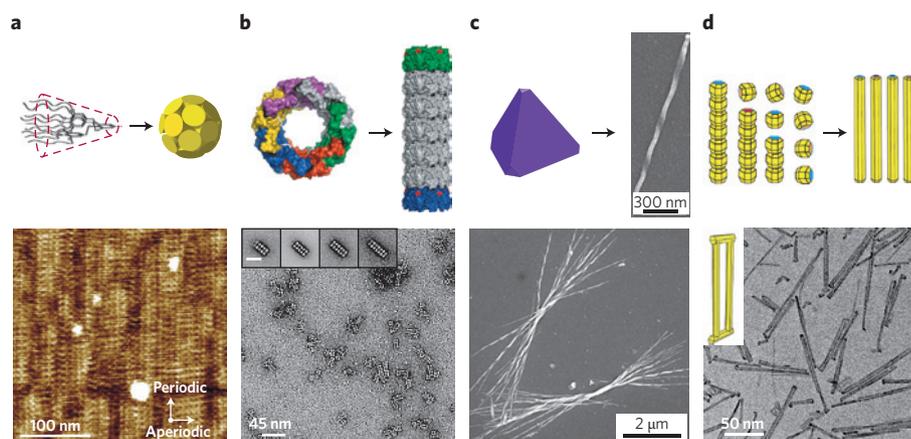


Figure 1 | Hierarchical self-assembly of molecules, proteins and nanoparticles. **a**, Cone-shaped monodendras assemble into spheres (top), which then form dendritic liquid quasicrystals⁸ (bottom). **b**, Hexameric ring structures self-assembled from protein building blocks (top left; different colours indicate different protein subunits) form short nanotubes⁶ (top right and bottom; capping protein rings are indicated in green and blue; the insets show, from left to right, average structures of nanotubes consisting of 4–7 rings; scale bar, 20 nm). **c**, Self-assembly of truncated semiconducting CdTe tetrahedra (top left) into twisted nanoribbons (top right), which in turn assemble into polydisperse bundles¹⁴ (bottom). **d**, ZnSe nanoparticles self-assemble into nanorods by oriented attachment (top). The nanorods then self-organize into couples by means of a self-limited process¹ (bottom). Figures reproduced with permission from: **a**, ref. 8, © 2004 NPG; **b**, ref. 6, © 2008 NAS; **c**, ref. 14, © 2010 AAAS; **d**, ref. 1, © 2014 NPG.

angle between the rods. Similar deformations have also been seen in at least two other cases of assembled nanostructures: twisted ribbons and short nanorod pairs^{2,14}. Hence, the distortions are not accidental or singular and would merit further attention. Their origin could be related to nanoscale mechanics and to the process of self-assembly. Quantitative description of the dihedral angles formed by different rods may turn out to be essential to find new synthetic routes to making chiral nanoscale structures and to better understand the intermolecular forces acting between semiconductor nanoparticles. □

Bongjun Yeom and Nicholas A. Kotov are at the Chemical Engineering Department, University of Michigan, 2300 Hayward Street,

Ann Arbor, Michigan 48109-2136, USA.
e-mail: kotov@umich.edu

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LIQUID CRYSTALS

Tangled loops and knots

Knot-shaped micrometric tubes embedded in a liquid crystal induce the formation of defect lines that loop around the knotted tubes to form knots.

William T. M. Irvine and Dustin Kleckner

The idea of tying a physical field — for example, a magnetic field — into a knot has long fascinated scientists. Unfortunately, tying a knot in a space-filling field is a more subtle affair than tying one's

shoelaces: the entire space-filling field has to twist to conform to the knotted region. Following over a century of speculation on how knotted physical fields might behave¹, technological advances in our ability to

manipulate, image and visualize fields in three dimensions are finally enabling the pursuit of knotted structures in the laboratory. Now, Ivan Smalyukh and colleagues demonstrate in *Nature Materials*

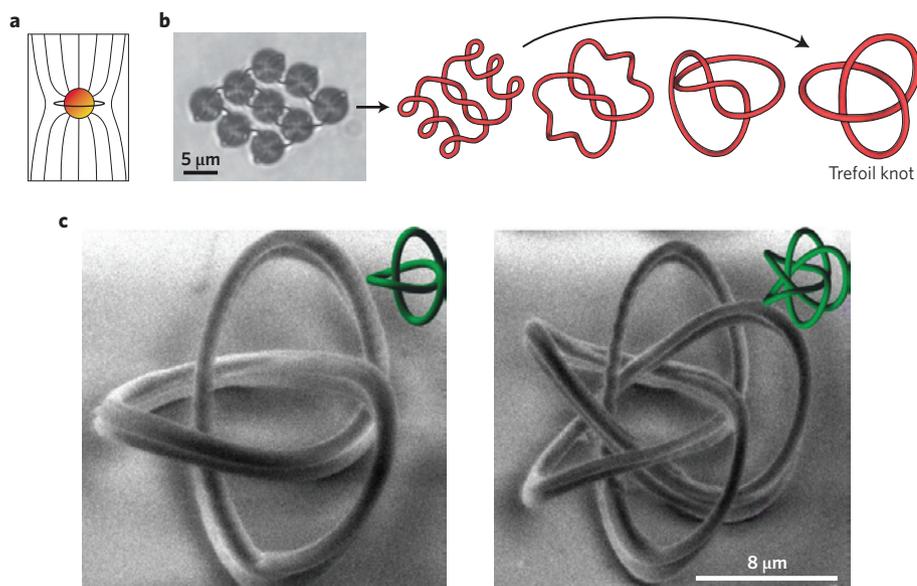


Figure 1 | Defect loops and knot-shaped microparticles. **a**, A ‘Saturn ring’ of defects surrounds a sphere immersed in a liquid crystal. **b**, By arranging spheres in the appropriate ordered configuration, Saturn rings can be connected into longer defect lines that have the topology of a trefoil knot³. **c**, Knot-shaped microparticles can be created by looping a laser beam through the hole of an imaginary torus in a light-sensitive polymer so as to set the desired knotted tubular loop, forming, for example, (3,2) (left) and (5,2) (right) torus knots². Figures reproduced with permission from: **a**, ref. 10, © 2013 NPG; **b**, ref. 5, © 2011 AAAS; **c**, ref. 2, © 2014 NPG.

that microscopic knotted loops made of rubber embedded in liquid crystals can coax defect fields to tie themselves into knots².

Liquid crystals typically consist of densely packed rod-like molecules oriented parallel to one another (nematic alignment), filling space along a so-called director field. The direction of the field depends on the molecular details of the liquid-crystal molecules, their interactions with the walls of the container and the container’s shape. In Smalyukh and co-workers’ study, the liquid crystals align preferentially in the direction perpendicular to the parallel walls of the container. However, the presence, in the bulk of the liquid, of an embedded object with a shape that is incompatible with the nematic alignment can locally frustrate the uniformity of the director field, leading to the formation of defect loops^{3,4} — that is, lines in space around which the director field rotates. For example, for an embedded spherical particle the defect loop takes the form of a so-called Saturn ring³ (Fig. 1a).

Recently, defect loops were tied into knots by carefully arranging collections of colloidal spheres so that their respective Saturn rings connect to each other and form a longer defect loop that has a knotted topology⁵ (Fig. 1b). However, the

microscopic particles that Smalyukh and co-authors use achieve this arrangement without the need for external manipulation and feedback. By tightly focusing a pulsed laser beam to locally set a light-sensitive polymer, the authors fabricated rigid rubber micrometric tubes shaped into knots (Fig. 1c). Then they chemically treated the surface of the knotted tubes so as to induce either tangential or

perpendicular anchoring of the liquid-crystal molecules in contact with the tube walls. When embedded in the liquid crystal, the knotted tubes induced the defect lines to loop around them, thus leading to inextricably entangled defect loops and colloidal knots (Fig. 2). By tuning the preferred surface anchoring — and thus the degree of incompatibility of the bulk alignment with the surface — Smalyukh and co-workers were able to control the arrangement of the defect lines around the tube. If perpendicular anchoring is favoured, two defect loops follow the surface of the tube along its entire length while slowly twisting around it (Fig. 2c). Instead, for tangential anchoring the defect loops latch onto the knotted tube at special points along its path and form a more complex arrangement. Hence, the combined ability to both fabricate microparticles with the desired topology and control the boundary conditions at their surface takes the practical engineering of knotted topologies in liquid crystals to a new level.

The possibility of tying knots within physical fields entered the collective imagination of scientists when Lord Kelvin conjectured that atoms were vortices in the electromagnetic ether¹. This elegant idea sought to replace the notion that atoms were solid objects, hypothesizing that they instead corresponded to knots tied in a field. Although not successful as a theory of atoms, the conjecture inspired many great developments: it was the origin of the field of knot mathematics, and has since re-emerged in the physics of turbulent flows and plasmas, and in exotic field theories. Being able to study knotted

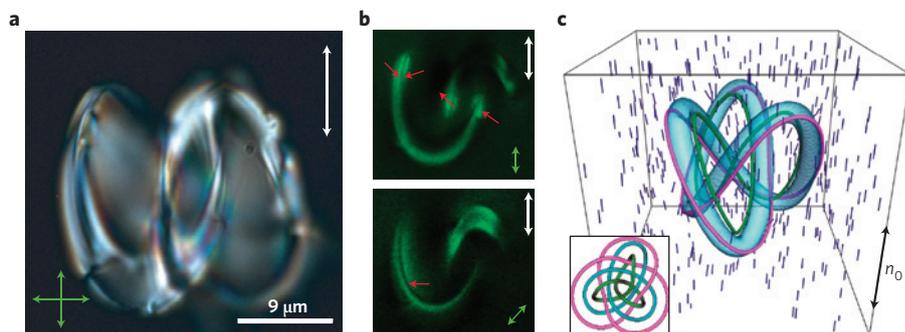


Figure 2 | Defect loops winding around knotted microparticles². **a, b**, Polarization-sensitive micrographs show the arrangement of liquid-crystal defects looping around a colloidal microparticle shaped as a trefoil knot (the directions of polarization are indicated by green double-headed arrows). Defect lines are shown by red arrows. The white double-headed arrows indicate the direction of the director field far from the microparticle. **c**, Computer-simulation snapshot of the director field (n_0) around a trefoil knot with perpendicular boundary conditions. Defect loops (green and magenta lines, which correspond to the top and bottom images in panel **b**, respectively) wind around the microparticle (blue). The inset is a schematic of the mutual entanglement of the microparticle knot and the defect knots.

fields experimentally should thus open exciting avenues, from the fundamental to the applied.

The knotted colloids of Smalyukh and colleagues bring the prospect of creating Kelvin-like knots in liquid crystals one step closer to reality. On the one hand, and unlike the recent realization of Kelvin vortex knots in simple fluids⁶, the liquid-crystal knots are statically pinned to the fabricated tubular structure — made possible by the structured nature of the fluid — and makes them more amenable to practical applications. Also, the knotted defect loops should give rise to directional interactions between the knotted tubes to which they are linked,

potentially offering enticing prospects for materials engineering³. On the other hand, the techniques employed by Smalyukh and co-authors may prove useful to further explore the interaction of liquid-crystal order with more complex topological obstructions. Could liquid-crystal knots be created in the absence of templating solid knots? Perhaps knot-shaped optical fields will provide an answer^{7–9}. If liquid-crystal knots could be templated by optical fields, might their structure shed light on the connection between knot theory and physical fields? Although the problems ahead are likely to be knotty, the prospects are enticing indeed. □

William T. M. Irvine and Dustin Kleckner are at the James Franck Institute, University of Chicago, Chicago, Illinois 60637, USA.
e-mail: wtmirvine@uchicago.edu

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GLUING GELS

A nanoparticle solution

Synthetic polymer gels with certain surface chemistries can be glued together by a simple and inexpensive method that uses commercially available silica nanoparticles. Biological tissues can also be joined by this nanotechnological route, eliminating the need for sutures, additional adhesives or chemical reactions.

Eric A. Appel and Oren A. Scherman

For over 200,000 years humans have been sticking things together¹, yet when it comes to gluing soft, squishy and slippery materials, such as hydrogels, strong adhesion is notoriously difficult to accomplish. Many adhesives are made of polymers because, unlike other materials, they ensure good contact between surfaces and they can dissipate energy under stress through rearrangement of their chains². Yet, polymer-based glues are often not water soluble or require *in situ* polymerization that can lead to unwanted side reactions and, as a consequence, significant alteration of the materials' properties. To circumvent these problems, scientists have exploited water-based molecular recognition motifs (for example, cyclodextrins³ and cucurbiturils⁴) or have taken hints from nature, developing mussel-inspired catechol-based adhesives^{5,6}.

Now, writing in *Nature*, Leibler and co-workers report a simple yet elegant method for 'gluing' hydrogels together that takes advantage of the unique adhesion properties of nanoparticles and stress dissipation properties of polymer chains (Fig. 1)⁷. The method builds on previous studies of self-healing rubbers⁸ and malleable thermosets⁹, and results in strong and rapid adhesion between two hydrogels at room temperature. It uses

inexpensive nanoparticles and works for a diverse range of polymeric hydrogels, making the process accessible to researchers

of different backgrounds and providing the potential for rapid translation to commercial applications.

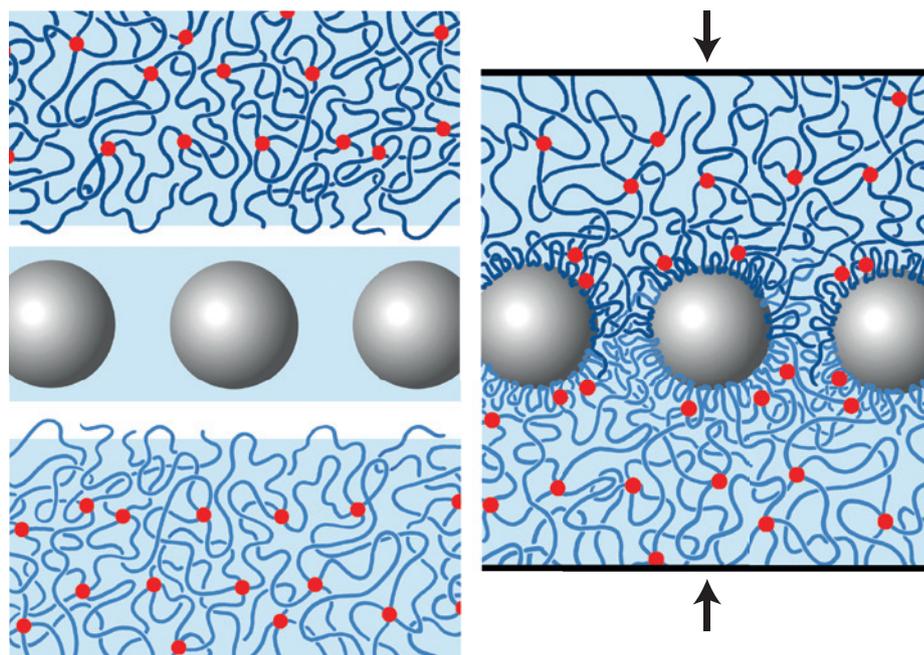


Figure 1 | Gluing gels with nanoparticles. A schematic illustration showing strong, yet dynamic and reversible gluing of gels by exploiting adsorption of polymer chains to the surface of the nanoparticles when pressure is applied (black arrows)⁷. The strongest adhesion is expected when the nanoparticle diameter is comparable to the distance between crosslinks (denoted by the red dots).