Title page

Transmission of Chirality Through Space and Across Length Scales

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Abstract

Chirality is a fundamental property and vital to chemistry, biology, physics and materials science. The ability to use asymmetry to operate molecular-level machines or macroscopically functional devices, or to give novel properties to materials, may address key challenges at the heart of the physical sciences. However, how chirality at one length scale can be translated to asymmetry at a different scale is largely not well understood. In this review we discuss systems where chiral information is translated across length scales and through space. A variety of synthetic systems involve the transmission of chiral information between the molecular-, meso-, and macro-scales. We show how fundamental stereochemical principles may be used to design and understand nano-scale chiral phenomena and highlight important recent advances relevant to nanotechnology. The survey reveals that while the study of stereochemistry on the nanoscale is a rich and dynamic area, our understanding of how to control and harness it and dial-up specific properties is still in its infancy. The long-term goals of controlling nano-scale chirality promises to be an exciting journey, revealing insight into biological mechanisms and providing new technologies based on dynamic physical properties.

Introduction

Biology uses chirality as a pervasive ‘design feature’ at all levels of organisation, from the monomers that compose genes, proteins, and membranes, to macroscopic structures such as sea shells and human appendages. Molecular asymmetry is so important to living systems that it is widely regarded as a biosignature; all known life uses monomers that share a common chiral sense, a phenomenon called biological homochirality.

In small molecules and common higher-order motifs, chirality is familiar and widely understood: chiral molecules are non-superimposable upon their mirror images. But chirality is a geometrical property independent of molecules or any other physical instantiation,[1] and it occurs in more esoteric forms. Physical forces such as photons, electrons, magnetic fields, and vortices may all be chiral. Some forces, such as magnetic fields and vortices, exhibit “false chirality” in that they are not time invariant and can be inverted by the combination of time reversal and spatial rotation.[2] The weak nuclear force is chiral, rendering the world fundamentally asymmetric. Consequently atoms themselves are chiral, meaning that enantiomers are predicted not to be strictly isoenergetic. The energetic difference between enantiomers is too small to be of consequence in chemical systems but is in principle measurable.[3,4]

Intuitively, some objects appear to be ‘more chiral’ than others. For example enantiomers distinguished by isotopic substitution seem ‘less chiral’ than enantiomers distinguished by more obviously different substituents. Such compounds are often ‘cryptochiral’ and can require specialised characterisation methods.[5] Attempts to quantify degrees of chirality date back to Guye in the 19th century.[6] This endeavour is unsurprisingly complicated and until theories are more fully developed it is best to define chirality in binary terms.[7,8]

The connection between molecular chirality and macroscopic chirality has been known since Pasteur showed that a single enantiomer crystal, when dissolved, could still rotate plane polarised light.[1,9] It is now obvious that both crystals and molecules can have asymmetry. The relay of chirality across length scales – how (+)-tartartic acid forms a single hemihedric crystal with dissymmetric facets inclined to the right or left – is only poorly understood. The study of chirality in even more complex architectures, such as inorganic nanoparticle assemblies, is therefore also in its infancy.

Living systems have dynamic structures which rely on the relay of chiral information across multiple length scales for function. Gene regulation involves the coiling and uncoiling of DNA and natural molecular motors use unidirectional motion to interconvert forms of energy. At the macroscopic level cucumber tendrils use helical coils to reach the sun and chiral seed pods open via mechanisms relying on helical shapes. A sense of asymmetry is vital to the operation of natural machines, allowing the directional rotary motion that drives ATP synthesis or bacterial flagella to be possible. Understanding the structure and function of these assemblies may reveal principles about how to design and assemble functional artificial systems.

Often, synthetic systems aim to emulate nature in their behaviour. However, unconstrained by biological homochirality, chemists are able to access materials and therefore mechanisms not observed in nature. Thus synthetic systems may amplify small enantiomeric excesses, or small asymmetric perturbations in systems based on achiral building blocks. Exploiting these principles in the rational design of potentially dynamic and responsive systems would provide access to new and valuable functional materials in chemistry, medicine and beyond. In this vein, artificial molecular machines have been extensively studied. It has become apparent that the major difficulty in operating molecular devices is not achieving motion, but instead in learning how to control this motion and use it to perform a function.[10–12] Key challenges include control over directionality, which requires a sense of asymmetry, and how to amplify the effect of the machines so that they can do work. As we will see below, a few early successes have already been demonstrated by exploiting chiral self-ordering phenomena that exert forces at the nano-, micro- and macroscopic levels.

In this review we survey synthetic systems where chiral information is ‘transmitted’ so that a local source of chirality influences the conformation or configuration of a remote site. We also discuss the transmission of chirality across length scales: how molecular-level chirality influences the meso- or macro-scale properties of a system. This includes examples from across the chemical literature which highlight common principles by which chirality can be transmitted and amplified, followed by a discussion on the emerging chiral nanotechnologies which rely on these and other principles.

We begin by briefly reviewing key stereochemical concepts and principles.[1] Molecular stereochemistry is generally well taught and intuitive to chemists, but the language of stereochemistry is extensive and precise. In some cases terms are controversial,[13] or good terms for certain aspects simply do not exist yet despite authoritative treatises.[1,14,15] We have tried to use as few specialist terms as possible and hope that readers will accept some imprecision in exchange for simplicity.

It is necessary here to distinguish between chirality at different length scales, as we move from the molecular to supramolecular to macroscopic scales. Here 'local' refers to monomers at the molecular scale, and arises from variation in conformation or configuration at the monomer level (Figure 1a,b). Global chirality refers to conformations at greater length scales such as in oligomers, polymers, supramolecular assemblies, and assemblies on surfaces or in liquid-crystalline structures, and is analogous to secondary or tertiary structure in proteins (Figure 1c). Finally, macroscopic chirality refers to micrometre or larger scales, including crystals and biological structures such as plant tendrils (Figure 1d). Clearly this distinction is imperfect, but useful for considering the influence of local chirality, such as isomerism at a single carbon atom, on the asymmetry of a larger system.

[Figure 1 near here]

The dynamic behaviour of chiral systems is important. In many cases configurational isomers are kinetically stable, as racemisation requires breaking a covalent bond. Kinetically stable chiral structures have been described as having 'permanent' chirality.[16] In contrast helical molecules and many other conformationally chiral species *may* have lower barriers to racemisation, as either enantiomer can be obtained by bond rotation. The distinction between permanent and transiently chiral species is a matter of degree; the energetic barriers to bond cleavage and bond rotation overlap considerably, and the crossing rate depends on conditions including temperature.[1] In general, permanently chiral species are easier to analyse than transiently chiral species; the introduction of dynamics to chiral systems can quickly complicate analysis.

A Mechanism for Transmitting Chirality

When enantiomers interact with another chiral species there is a difference between the energy of the two interactions and they become diastereomeric to one another. The energetic difference between diastereomeric interactions is essential to many of the examples reviewed here and is illustrated (Figure 1e) by the reaction of a pair of enantiomers with an enantiomerically-pure chiral molecule. The enantiomers interact with the chiral reagent with different energies. They therefore react at a different rate, via diastereomeric transition states, to give a mixture of two energetically, physically, and chemically distinct diastereoisomers.

This principle is general and applies to any interaction between chiral species including non-covalent interactions, conformationally or transiently chiral species, and interactions with physical forces such as circularly polarised light. For example, a pair of enantiomeric helices becomes diastereomeric by interaction with a single enantiomer chiral reagent (Figure 1f). As a result the two helical screw senses are no longer energetically equivalent and one sense is favoured over the other. For helices with a low barrier to interconversion, the system could respond to chiral stimuli by preferentially adopting one screw sense. The degree to which one enantiomer is favoured over another can be quantified as 'enantiomeric excess' (ee), defined as the percentage excess of the major enantiomer over the racemate.[1]

The energies of diastereomeric interactions can have significant consequences even in simple systems. In samples that are neither racemic (0% ee) nor enantiomerically pure (100% ee), i.e. in scalemic samples, homochiral and heterochiral dimers (or higher oligomers) form which are diastereomeric and different in energy. Depending on the relative strength of these interactions, the system may preferentially form racemic or conglomerate domains (Figure 1g).[1] The energy difference between homo- and heterochiral interactions leads to non-linear effects in asymmetric catalysis,[17] changes in enantiomeric composition during crystallisation, and has been implicated in the origins of biological homochirality.[18]

Diastereomeric interactions can be used to transmit and amplify chirality, and exploiting this concept is the basis of much of the work covered in this review.

Transmission of Chirality In Covalent and Supramolecular Structures

The transmission of chirality within conformationally constrained polymers, foldamers and supramolecular assemblies has been widely explored (Figure 2).[19–28] Whilst supramolecular and polymeric systems composed of chiral monomers are inherently chiral, achiral monomers may also preferentially adopt stable chiral conformations when forming higher order architectures. Helical conformations are pervasive and appear to be the most common structural element for the transmission of chirality. Well-defined, rigid helices allow the robust transmission of information in one dimension along the backbone, which can be harnessed for function.

Perhaps the simplest demonstration of the transmission of chirality across length scales is the formation of globally chiral supramolecular structures from chiral monomers. In pioneering studies, Green and co-workers demonstrated that isocyanate polymers are highly sensitive to local chirality: monomers rendered chiral by a single deuterium label gave polymers with high optical activity arising from the helical chromophore (Figure 2a).[29] Although each residue imparts only a tiny conformational bias, a high screw-sense preference is observed. In contrast, polymers of achiral isocyanate monomers adopt helical conformations with no screw-sense preference. Non-covalent supramolecular structures can display the same sensitivity to isotopic substitution, as described by Meijer and co-workers (Figure 2a).[30]

Globally chiral supramolecular structures commonly show high fidelity of chiral transmission. While helices are the most widely studied motif other structures are known.[31] The global conformation of these structures is frequently mediated by, and highly sensitive to, hydrogen bonding, π-stacking, chiral guests, and solvent interactions.[19–28,32] Environmental sensitivity of this kind can give rise to numerous dynamic chiral supramolecular architectures with induction, switching, or ‘memory’ of a screw-sense preference.[19–21,23–26,28,33,34]

The strong chiral recognition in some supramolecular assemblies can even lead to spontaneous mirror symmetry breaking processes.[35–37] Here, systems composed of achiral or racemic monomers are driven to a non-racemic state in the absence of a chiral influence. This seems to require the interaction of multiple helical assemblies through processes analogous to nucleation in crystallisation.[38] A few examples even involve the handedness of the initial ‘seed’ being selected by physical vortices, which are false chiral sources.[36,37]

Mechanisms for the transmission of chirality in one-dimensional systems can illuminate the behaviour of higher-order materials. In particular, two common effects seen in individual polymers have analogues in higher-order assemblies. The “Sergeants and Soldiers” (SS) effect occurs when achiral monomers interact with a small number of chiral monomers which determine the global chiral conformation. The “Majority Rules” (MR) effect occurs when the global supramolecular structure is determined by a small imbalance in the directing ability of the monomers present, such as a small enantiomeric excess (Figure 2b). Both effects have been used by Green and co-workers to control the global helical sense of polyisocyanates[39,40] and have been observed in a variety of covalent and supramolecular polymers and foldamers.[19–21,23–26,28]

Both the MR and SS effects constitute strong nonlinear responses of polymer structure to small chiral biases among monomers. It may be difficult to rationalise these effects by simple monomer interactions, but the work of Meijer has shown that they can be understood by considering the energetic cost of screw-sense inversions or incorporation of mismatched monomers to a growing chain.[30,41] Thermodynamic models can account for both SS and MR effects in cooperative supramolecular polymerisation and offer insight into the origin of chiral amplification.[42]

These effects allow small sources of local chirality to be amplified to the global level and a route to dynamic behavior such as helix inversion in response to stimuli: a small number of monomers containing switches can control the global conformation. This is potentially important for the precise design of functional materials and has been exploited in higher-order materials such as liquid crystals (see below).[43–45]

The SS and MR effects rely on chiral monomers distributed more or less evenly throughout a polymer. To understand how much influence a single chiral monomer can have on global chirality numerous researchers have studied small foldamers.[46] These are typically short (n < 20) oligomers of achiral monomers containing a single chiral residue. In particular, Clayden and co-workers have explicitly investigated the limits of and prerequisites for the transfer of chiral information down a chain. A chiral influence at one end of the oligomer can induce a preference for one helical sense, providing a mechanism for transmitting chiral information along the oligomer.[47–49] This has been called the domino effect.[50] Using Aib (2-aminoisobutyric acid) oligomers which form rigid helices that rapidly interconvert in solution,[51] Clayden *et al*. have demonstrated and exploited highly selective control over screw-sense preference.[52]

A global screw-sense imparted via the domino effect can also be used to induce local chirality. An Aib oligomer with a chiral bis-amino acid residue at its terminus induces diastereoselectivity in a reaction at a prochiral site about 4 nm from the source of chirality (Figure 2c).[48] The global screw-sense preference can be switched by incorporating a light-driven azobenzene moiety, allowing controlled transitions between ‘on’ (induction of preferred helical sense) or ‘off’ (negligible induction of preferred helical sense) states. A switchable oligomer of this kind has been embedded in a bilayer membrane to model and understand the dynamics of helical membrane proteins.[49]

Molecular switches and motors have also been harnessed to induce helical deformations on a larger scale.[53] Feringa has demonstrated that polyisocyanate helicity can be controlled by attachment to a unidirectional 4-state rotary molecular motor (Figure 2d). Controlled switching from one state to another using heat and light allows selection of either the *M* or *P*-helical sense or a racemic mixture of helicies.[54,55] On a smaller scale, a unidirectional motor has been used to control the conformation of a double helix constructed from oligobipyridyl ligands and metal ions.[56] These examples use light as a control element: this is a non-invasive source of chirality inversion with high spatial and temporal resolution compared to chemical methods.

Together these studies reveal a coherent set of principles by which chiral information on the molecular level can be amplified to higher levels of assembly or transmitted through large molecules. Key challenges remain; rationally designing molecules capable of a desired conformational response is still difficult. Responsive materials that enable chiral signals to be transmitted or amplified can be expected to yield ‘smarter’ molecules capable of dynamic responses to environmental stimuli in the future. The non-invasive and reversible control of molecular conformation may mimic aspects of biological information processing such as signal transduction, and provide a valuable toolbox for the operation of future generations of synthetic molecular machines and synthetic biology.[52,53]

[Figure 2 near here]

Transmission of Chirality in Liquid Crystals and On Surfaces

The transmission of chirality between molecules is enhanced in phases where a greater number of hierarchical interactions are present. Molecules assembled at surfaces or interfaces, or in liquid crystalline phases, show intriguing stereochemical phenomena throughout the ordered phase, providing additional mechanisms for information transfer.

Liquid Crystalline Materials

The combination of dynamic, fluid properties with a high degree of organisation renders liquid crystals (LCs) highly sensitive to external stimuli and dopants. The higher degree of order in LCs compared to the solution phase can enhance the fidelity of chiral transmission, allow long-range order to be induced, and give rise to dynamic and responsive materials.

Chirality in LCs may arise at the global level in the transition from a nematic phase to a chiral nematic phase by using either chiral monomers, physical confinement of the alignment layers, or chiral dopants (Figure 3a).[57] The chirality of LC phases has been covered in excellent reviews,[16,58,59] including formation of conglomerate phases and SS type behavior where a chiral dopant induces a single homochiral LC domain.[60]

[Figure 3 near here]

Interconverting polyisocyanate helices can form a lyotropic (solvent-solute) LC phase where chiral dopants non-covalently impart a slight screw-sense preference. The preference is amplified by the liquid crystal matrix itself: helices containing screw-sense inversion nodes are disfavoured within the LC, resulting in helices that exhibit a single screw sense throughout their entire length.[61,62] The higher order of the LC phase also allowed Green and co-workers to explore ‘chiral conflict’,[63] where polymers substituted with different chiral side chains compete for control of the global helical screw-sense preference. Since the competing structures are not enantiomers, the energetic preferences for a particular helix handedness are not equal in magnitude and vary with temperature. In an LC matrix, this allows the formation of thermally-switchable chiral nematic phases.

The inclusion of chiral photoswitches as ‘sergeants’ to direct otherwise achiral nematic LC phases in response to irradiation is an increasingly powerful approach, with manipulation of both helical sense and director orientation being possible.[64]

A remarkable demonstration of LC photoswitching being harnessed to do mechanical work was reported by Feringa and co-workers in 2006.[65] On doping a liquid crystal with a light-driven molecular motor, the liquid crystal texture undergoes dynamic rearrangement upon irradiation. The unidirectional motion of the chiral motor is transmitted and amplified via the LC phase and used to rotate a glass rod, which is 10,000 times larger than the motor itself.

Katsonis and co-workers reported macroscopic helical deformations using a design strategy where molecular movement within chiral LC materials is translated across length scales

(Figure 3b). These form the basis of macroscopically functional materials and can mimic mechanisms of movement seen in plants.[66] Nematic LCs polymerised to form soft elastomeric materials and containing a chiral dopant selectively form right- or left-handed domains, which display strong coupling between orientational order and mechanical strain. Incorporation of photoswitchable azobenzene molecules into the network allows the LC order to be disrupted on irradiation with light and results in shape changes at the macroscopic level by the anisotropic deformation of the whole material. Light-induced shrinkage occurs primarily along one face of the helix, while expansion occurs along the other. Three sources of asymmetry, both at the molecular and macroscopic levels, contribute to shape generation and actuation: 1) the absolute sense of twistedness of monomers in the cell, 2) a polymer density gradient formed during polymerisation because the LC cell is irradiated from one side and 3) the angle at which the ribbon is cut. Ribbons cut from the film curl into a variety of chiral and achiral shapes, and different shapes exhibit different mechanical movements when irradiated.

The integration of functional molecules into higher order materials such as liquid crystals enables the ability to perform work at the macroscopic level using nano-scale building blocks. It appears clear that a sense of asymmetry is vital to such operations, but the asymmetry does not necessarily need to derive from the use of chiral building blocks. For example, the microfibrication process itself can be used to produce functional mirror image LC elastomers.[67] Harnessing the harmonised motion of nano-scale machines has been long anticipated and sets the stage for advances in artificial muscles, microfluidics and soft robotics and undoubtedly additional future architectures which can mimic biological systems and materials that are not yet even anticipated.[10–12]

Chiral Transmission at Interfaces and On Surfaces

The presence of an interface changes the behavior of adsorbed molecules by altering intermolecular interactions. Confinement to a two-dimensional surface can also break the symmetry of achiral structures, rendering them chiral.[68] The analysis of molecules assembled at surfaces can be more complex than in solution; in particular, circular dichroism spectroscopy can be confounded by artefacts, complicating analysis. In contrast to crystallisation in three dimensions, the formation of homochiral (conglomerate) domains rather than heterochiral (racemic) domains is more common during two-dimensional assembly on account of the reduced number of symmetry elements present.[58] The study of self-assembly at interfaces and surfaces can aid our understanding of three-dimensional crystals and crystallisation processes[69] and can be used for the synthesis of otherwise difficult-to-obtain chiral materials, such as in the synthesis of homochiral graphene nanoribbons.[70]

Direct analogues of the SS effect have been observed in two-dimensional assemblies, using mechanisms analogous to those seen in polymers and LCs.[71,72] However at surfaces, both SS and MR effects can be obtained via different mechanisms to those discussed above.[73,74] For example, racemic heptahelicene can exhibit a MR-like effect that relies on the sequestration of the major enantiomer into an amorphous domain. Racemic heptahelicene does not undergo spontaneous resolution on a Cu(111) surface, but forms a 1:1 mixture of two enantiomorphic domains (λ and ρ). Each contains a racemic mixture of helicenes (Figure 3c).[74] Deposition of scalemic helicene results in strong chiral amplification, giving a single enantiomorph when ee > 8%. This arises because the excess major enantiomer forms an amorphous residual domain, and the interactions of edges of this domain with edges of the λ and ρ domains are diastereomeric to one another. This small chiral bias at the interface of the λ or ρ domain enforces the local adoption of a single domain, which is amplified across hundreds of nanometres.

As well as acting as a simple boundary, the surface itself may be rendered chiral. In the adsorption of aspartic acid to an achiral Cu(III) surface, small enantiomeric excesses in the gas phase gave higher levels of enantiomeric enrichment in the adsorbate. It was tentatively proposed that this effect originates from the preferential formation of homochiral clusters, but may derive from chiral imprinting of the surface.[75] Chiral imprinting involves the reordering of the surface via binding of chiral molecules. This creates new diastereomeric interactions and is expected to induce non-linear effects.[76–79] Similarly, deposition on a surface with inherent chirality has been explored in ‘chiral surface explosions’, where autocatalytic and enantioselective mechanisms operate to amplify chirality.[80]

Transmission of Chirality in Nanoscale Architectures

The emergence of chirality in nanoparticles and related nanoscale materials is less established than in traditional organic systems, but the same core principles described above should be applicable to their development. At present the SS and MR effects, so powerful in the development of switchable polymers and LCs, are less well known in nanoparticle assemblies. Their application in this area would open new possibilities for the development of dynamic, responsive inorganic materials.

The basic geometric requirements for chirality are the same in nanoparticles as in molecular systems. Commonly, individual nanoparticles are rendered chiral by the configuration or arrangement of ligands at the nanoparticle surface.[81–83] It is also possible for nanoparticles to have intrinsic chirality associated with the core. This may be induced by chiral ligands: graphitic materials, for example, can adopt a chiral buckled shape when bound to chiral ligands.[84,85] Much like 2D metal surfaces, metal nanoparticles can be ‘imprinted’ by a chiral molecular template.[86] Atomically well-defined metal clusters can have chiral configurations without any need for chiral ligands.[87,88] Similarly, nanoparticles can crystallise in chiral symmetry groups, in direct analogy to macroscopically chiral crystals.[89] As with macroscopic crystals, a source of chirality is required to induce an ee.

Both chiral and achiral nanoparticles can assemble into globally chiral structures. While intrinsic global conformational preferences are known,[82,83,90] it is far more common to use a template or scaffold.[86,91] Templates can impart a wide variety of geometries to nanoparticle assemblies and commonly provide both a conformational preference and a bias towards one enantiomorph. Templates include supramolecular structures,[92,93] chiral fields such as liquid crystals,[94,95] and macromolecules such as proteins and polynucleotides (Figure 4c).[96–101] Through these methods we can access not only helices[92–96,98,100–103] but also tetrahedral[97,99,104,105] and more complex geometries.[106,107]

Conversely, nanoscale materials can be used to template the synthesis of macroscopic chiral materials. MacLachlan and co-workers have used nanocrystalline cellulose (Figure 4a) to template formation of mesoporous silica films.[108] Nanocrystalline cellulose self-assembles into a chiral nematic phase which imprints long-range chiral structure onto silica, ultimately transferring molecular chirality from D-glucose monomers to the global structure of an inorganic chiral material. The resultant silica can in turn be used as a template to direct the assembly of silver nanoparticles into chiral supramolecular structures.[109]

[Figure 4 near here]

More exotic sources of chiral bias have been used to direct the self-assembly of chiral inorganic materials. Kotov and coworkers have explored the self-assembly of superconducting quantum dots into macroscopically chiral ribbons.[82] Tetrahedral CdTe semiconductor nanoparticles capped with achiral ligands are chiral due to different truncations of the nanoparticle at each vertex. In a system in which light is the control element, the left-handed nanoparticles absorb left-handed circularly polarised light more effectively than do right-handed nanoparticles (and vice-versa). Consequently the ligands of one enantiomorph of the nanoparticles can be selectively photooxidised. The subsequent self-assembly of the ligand-free nanoparticles into helical nanoribbons is sensitive to the anisotropy of nanoparticle interactions and there is a strong screw-sense preference. Light absorption for nanoparticles of one handedness is therefore translated to chirality on the mesoscale with significant enantiomeric excess (Figure 4d).[110]

Kotov *et al.* have also reported a ‘top-down’ approach to producing global chirality in nanoparticle assemblies.[111] Working with achiral layered poly(dimethylsiloxane) coated in nanoparticles they found several materials which exhibit chiroptical activity in response to macroscopic deformations (Figure 4b). Twisting the material prior to depositing the nanoparticles imparts long-range chiral order to the pattern of deposited particles when the material is untwisted: the material ‘remembers’ the macroscopic stimulus. Further, the memory of long-range order and macroscopic deformations can be reversibly exaggerated by stretching the material.

Magnetic fields can be used to direct the assembly of nanoparticles,[91] and under the correct conditions can produce chiral structures. Singh *et al.* reported the assembly of magnetic nanoparticles into enantiomorphic helices in the presence of a magnetic field.[90] Careful tuning of the experimental conditions led to the formation of long-range (1 mm^2) single-enantiomorph domains containing helices of only one screw sense, albeit with short stretches of helical inversion. The screw sense obtained varied randomly between experiments, as is seen in crystalline systems, suggesting a high fidelity of chiral transmission between helical assemblies.

Vortices, a source of ‘false chirality’, can induce chirality in graphene oxide aggregates. The handedness of the mechanical vortex in turn can be transferred to other molecules, such as porphyrin derivatives that associate with graphene oxide through non-covalent interactions to induce measurable CD signals. Stirred solutions of graphene oxide could also be deposited on quartz to capture the transient, vortex-induced chirality of graphene oxide assemblies, providing an unusual route to chiral nanomaterials.[112]

As with organic polymers, developing environmentally responsive and switchable materials is a priority in this field.[91] Light is a pervasive control element: an approach reported by Liu and co-workers involves photoswitching between chiroptically active and inactive states in gold nanorods. By functionalising a DNA scaffold with azobenzene-modified oligonucleotides, the scaffold can be switched between ‘locked’ and ‘unlocked’ states and amplifies azobenzene isomerisation, with a molecular length change of ~ 3.5 Å, to the large scale movement of the entire scaffold of ~ 30 nm.[113] Furthermore, the same group has harnessed the chemistry and chirality of the DNA template to give rise to motor-like behaviour. Here, the sequential addition and removal of individual DNA strands acts as a chemical fuel for the directional motion of a gold nanorod assembly.[114] Inspired by comparisons to the motors of biology, which are powered by chemical gradients or ATP hydrolysis, the production and refinement of chemically-driven motors remains an exciting, but very challenging, field.[12]

The study of chiral nanoparticles and their assemblies is young compared to the study of organic systems.[91] In contrast to polymeric systems, the dominant approach to chiral nanoparticle assemblies seems to be the use of chiral templates to direct assembly rather than self-organisation based on intrinsic conformational preferences. As more examples of dynamic, environmentally responsive chiral nanoparticle assemblies emerge we can expect to see new materials with functions inaccessible to purely organic systems.

Conclusion and outlook

Chirality is a natural phenomenon and there is little question of its importance to chemistry, but understanding how chiral species interact and assemble is increasingly important to problems in biology, materials science and physics as well. Our survey of how chirality may be transmitted through space and across length scales reveals that stereochemistry continues to be a rich and dynamic subject at the heart of the physical sciences.

The development of dynamic and kinetically controlled systems which rely on an element of asymmetry are increasingly important. Exquisite control can be achieved in the use of light-controlled molecular motors and switches within purely organic materials. In contrast, the study of chiral nanoparticles and their assemblies is young; dynamic behavior in architectures at this scale is perhaps the next frontier, and would offer function that is simply inaccessible otherwise. We need new tools to produce and study such systems, allowing time-resolved analysis of chiral materials on both the ensemble and single-particle levels.

Before we can access highly dynamic structures, the principles of chiral transmission must be established. We have good understanding of the chirality of organic molecules and, to a large extent, their assemblies across various architectures. An increased understanding of how the intrinsic, ‘local’ chirality of nanoscale species can be translated into their chiral assemblies, their ‘global’ or even ‘macroscopic’ chirality would be most valuable and could serve as the basis of new understanding and the discovery of new mechanisms and materials.

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References

1. Eliel, E. L. & Wilen, S. H. *Stereochemistry of Organic Compounds*. (Wiley, 1994).
2. Feringa, B. L. & van Delden, R. A. Absolute Asymmetric Synthesis: The Origin, Control, and Amplification of Chirality. *Angew. Chemie Int. Ed.* **38,** 3418–3438 (1999).
3. Fábri, C., Horný, Ľ. & Quack, M. Tunneling and Parity Violation in Trisulfane (HSSSH): An Almost Ideal Molecule for Detecting Parity Violation in Chiral Molecules. *ChemPhysChem* **16,** 3584–3589 (2015).
4. Quack, M. How Important is Parity Violation for Molecular and Biomolecular Chirality? *Angew. Chemie Int. Ed.* **41,** 4618–4630 (2002).
5. Kawasaki, T. *et al.* Discrimination of cryptochirality in chiral isotactic polystyrene by asymmetric autocatalysis. *Chem. Commun.* 5621–5623 (2009).
6. Guye, P.-A. Influence de la constitution chimique des dérivés du carbone sur le sens et les variations de leur pouvoir rotatoire. *C.R. Hebd. Seances Acad. Sci.* **110,** 714 (1890).
7. Buda, A. B., der Heyde, T. A. & Mislow, K. On Quantifying Chirality. *Angew. Chemie Int. Ed. English* **31,** 989–1007 (1992).
8. Millar, G., Weinberg, N. & Mislow, K. On the Osipov–Pickup–Dunmur chirality index: why pseudoscalar functions are generally unsuitable to quantify chirality. *Mol. Phys.* **103,** 2769–2772 (2005).

9. Pasteur, M. L. L. Recherches sur les propriétés spécifiques des deux acides qui composent l’acide racémique. *Ann. Chim. Phys.* **28,** 56–117 (1850).

10. Browne, W. R. & Feringa, B. L. Making molecular machines work. *Nat. Nanotechnol.* **1,** 25–35 (2006).

11. Coskun, A., Banaszak, M., Astumian, R. D., Stoddart, J. F. & Grzybowski, B. A. Great expectations: can artificial molecular machines deliver on their promise? *Chem. Soc. Rev.* **41,** 19–30 (2012).

12. Kay, E. R. & Leigh, D. A. Rise of the Molecular Machines. *Angew. Chemie Int. Ed.* **54,** 10080–10088 (2015).

13. Brewster, J. H. Racemic, scalemic, holemic. *Chem. Eng. News* **70,** 2–3 (1992).

14. Eliel, E. L. Infelicitous stereochemical nomenclature. *Chirality* **9,** 428–430 (1997).

15. Helmchen, G. Glossary of problematic terms in organic stereochemistry. *Enantiomer* **2,** 315–318 (1997).

16. Tschierske, C. & Ungar, G. Mirror Symmetry Breaking by Chirality Synchronisation in Liquids and Liquid Crystals of Achiral Molecules. *ChemPhysChem* **17,** 9–26 (2016).

17. Satyanarayana, T., Abraham, S. & Kagan, H. B. Nonlinear effects in asymmetric catalysis. *Angew. Chem. Int. Ed.* **48,** 456–494 (2009).

18. Blackmond, D. G. & Klussmann, M. Spoilt for choice: assessing phase behavior models for the evolution of homochirality. *Chem. Commun.* 3990–6 (2007).

19. Yashima, E., Maeda, K. & Nishimura, T. Detection and Amplification of Chirality by Helical Polymers. *Chem. - A Eur. J.* **10,** 42–51 (2004).

20. Palmans, A. R. A. & Meijer, E. W. Amplification of chirality in dynamic supramolecular aggregates. *Angew. Chemie - Int. Ed.* **46,** 8948–8968 (2007).

21. Pijper, D. & Feringa, B. L. Control of dynamic helicity at the macro- and supramolecular level. *Soft Matter* **4,** 1349 (2008).

22. Sorrenti, A., Illa, O. & Ortuno, R. M. Amphiphiles in aqueous solution: well beyond a soap bubble. *Chem. Soc. Rev.* **42,** 8200–8219 (2013).

23. Nakano, T. & Okamoto, Y. Synthetic helical polymers: Conformation and function. *Chem. Rev.* **101,** 4013–4038 (2001).

24. Cornelissen, J. J. L. M., Rowan, A. E., Nolte, R. J. M. & Sommerdijk, N. A. J. M. Chiral architectures from macromolecular building blocks. *Chem. Rev.* **101,** 4039–4070 (2001).

25. Hembury, G. A., Borovkov, V. V. & Inoue, Y. Chirality-sensing supramolecular systems. *Chem. Rev.* **108,** 1–73 (2008).

26. Liu, M., Zhang, L. & Wang, T. Supramolecular Chirality in Self-Assembled Systems. *Chem. Rev.* **115,** 7304–7397 (2015).

27. Elemans, J. A. A. W., Rowan, A. E. & Nolte, R. J. M. Mastering molecular matter. Supramolecular architectures by hierarchical self-assembly. *J. Mater. Chem.* **13,** 2661 (2003).

28. Yashima, E. *et al.* Supramolecular Helical Systems: Helical Assemblies of Small

Molecules, Foldamers, and Polymers with Chiral Amplification and Their Functions. *Chem. Rev.* **116,** 13752–13990 (2016).

29. Green, M. M., Andreola, C., Munoz, B., Reidy, M. P. & Zero, K. Macromolecular stereochemistry: a cooperative deuterium isotope effect leading to a large optical rotation. *J. Am. Chem. Soc.* **110,** 4063–4065 (1988).

30. Cantekin, S., Balkenende, D. W. R., Smulders, M. M. J., Palmans, A. R. A. & Meijer, E. W. The effect of isotopic substitution on the chirality of a self-assembled helix. *Nat. Chem.* **3,** 42–6 (2011).

31. Yin, P. *et al.* Chiral recognition and selection during the self-assembly process of protein-mimic macroanions. *Nat. Commun.* **6,** 6475 (2015).

32. De Greef, T. F. A. *et al.* Supramolecular polymerization. *Chem. Rev.* **109,** 5687–5754 (2009).

33. Shimomura, K., Ikai, T., Kanoh, S., Yashima, E. & Maeda, K. Switchable enantioseparation based on macromolecular memory of a helical polyacetylene in the solid state. *Nat. Chem.* **6,** 429–34 (2014).

34. Ohta, E. *et al.* Redox-responsive molecular helices with highly condensed π-clouds. *Nat. Chem.* **3,** 68–73 (2010).

35. Azeroual, S. *et al.* Mirror symmetry breaking and chiral amplification in foldamer-based supramolecular helical aggregates. *Chem. Commun.* **48,** 2292 (2012).

36. Ribó, J. M., Crusats, J., Sagués, F., Claret, J. & Rubires, R. Chiral Sign Induction by Vortices During the Formation of Mesophases in Stirred Solutions. *Science* **292,** 2063–2066 (2001).

37. Micali, N. *et al.* Selection of supramolecular chirality by application of rotational and magnetic forces. *Nat. Chem.* **4,** 201–207 (2012).

38. Noorduin, W. L. *et al.* Complete chiral symmetry breaking of an amino acid derivative directed by circularly polarized light. *Nat. Chem.* **1,** 729–732 (2009).

39. Green, M. M. *et al.* Macromolecular stereochemistry: the out-of-proportion influence of optically active comonomers on the conformational characteristics of polyisocyanates. The sergeants and soldiers experiment. *J. Am. Chem. Soc.* **111,** 6452–6454 (1989).

40. Green, M. M., Garetz, B. a, Munoz, B. & Chang, H. Majority Rules in the Copolymerization of Mirror Image Isomers. *J. Am. Chem. Soc.* **117,** 4181–4182 (1995).

41. Smulders, M. M. J. *et al.* Probing the Limits of the Majority-Rules Principle in a Dynamic Supramolecular Polymer. *J. Am. Chem. Soc.* **132,** 620–626 (2010).

42. Markvoort, A. J. *et al.* Theoretical models of nonlinear effects in two-component cooperative supramolecular copolymerizations. *Nat. Commun.* **2,** 509 (2011).

43. Ajayaghosh, A., Varghese, R., Mahesh, S. & Praveen, V. K. From vesicles to helical nanotubes: A sergeant-and-soldiers effect in the self-assembly of oligo(p-phenyleneethynylene)s. *Angew. Chemie - Int. Ed.* **45,** 7729–7732 (2006).

44. Arias, S., Bergueiro, J., Freire, F., Quiñoá, E. & Riguera, R. Chiral Nanostructures from Helical Copolymer-Metal Complexes: Tunable Cation-π Interactions and Sergeants and Soldiers Effect. *Small* **12,** 238–244 (2016).

45. Li, J., Schuster, G. B., Cheon, K. S., Green, M. M. & Selinger, J. V. Switching a helical polymer between mirror images using circularly polarized light. *J. Am. Chem. Soc.* **122,** 2603–2612 (2000).

46. Noe, C. R., Knollmüller, M. & Ettmayer, P. Paraformaldehyde as Possible Chirality Amplifier. *Angew. Chemie Int. Ed. English* **27,** 1379–1381 (1988).

47. Boddaert, T., Solà, J., Helliwell, M. & Clayden, J. Chemical communication: conductors and insulators of screw-sense preference between helical oligo(aminoisobutyric acid) domains. *Chem. Commun. (Camb).* **48,** 3397–9 (2012).

48. Byrne, L. *et al.* Foldamer-mediated remote stereocontrol: >1,60 asymmetric induction. *Angew. Chemie - Int. Ed.* **53,** 151–155 (2014).

49. De Poli, M. *et al.* Conformational photoswitching of a synthetic peptide foldamer bound within a phospholipid bilayer. *Science* **352,** 575–580 (2016).

50. Inai, Y. *et al.* Induction of one-handed helical screw sense in achiral peptide through the domino effect based on interacting its N-terminal amino group with chiral carboxylic acid. *J. Am. Chem. Soc.* **122,** 11731–11732 (2000).

51. Hummel, R.-P., Toniolo, C. & Jung, G. Conformational Transitions between Enantiomeric 310-Helices. *Angew. Chemie Int. Ed. English* **26,** 1150–1152 (1987).

52. Le Bailly, B. A. F. & Clayden, J. Dynamic foldamer chemistry. *Chem. Commun.* **2,** 303 (2016).

53. Yu, Z. & Hecht, S. Remote control over folding by light. *Chem. Commun.* **52,** 6639–6653 (2016).

54. Pijper, D. & Feringa, B. L. Molecular transmission: Controlling the twist sense of a helical polymer with a single light-driven molecular motor. *Angew. Chemie - Int. Ed.* **46,** 3693–3696 (2007).

55. Pijper, D., Jongejan, M. G. M., Meetsma, A. & Feringa, B. L. Light-controlled supramolecular helicity of a liquid crystalline phase using a helical polymer functionalized with a single chiroptical molecular switch. *J. Am. Chem. Soc.* **130,** 4541–4552 (2008).

56. Zhao, D., van Leeuwen, T., Cheng, J. & Feringa, B. L. Dynamic control of chirality and self-assembly of double-stranded helicates with light. *Nat. Chem.* **9,** 250–256 (2017).

57. Eelkema, R. & Feringa, B. L. Amplification of chirality in liquid crystals. *Org. Biomol. Chem.* **4,** 3729–3745 (2006).

58. Pérez-García, L. & Amabilino, D. B. Spontaneous resolution , whence and whither : from enantiomorphic solids to chiral liquid crystals , monolayers and macro- and supra-molecular polymers and assemblies. *Chem. Soc. Rev.* **36,** 941–967 (2007).

59. Reddy, R. A. & Tschierske, C. Bent-core liquid crystals : polar order , superstructural chirality and spontaneous desymmetrisation in soft matter systems. *J. Mater. Chem.* **16,** 907–961 (2006).

60. Dressel, C., Reppe, T., Prehm, M., Brautzsch, M. & Tschierske, C. Chiral self-sorting and amplification in isotropic liquids of achiral molecules. *Nat. Chem.* **6,** 971–7 (2014).

61. Green, M. M. *et al.* Mechanism of the Transformation of a Stiff Polymer Lyotropic Nematic Liquid Crystal to the Cholesteric State by Dopant-Mediated Chiral

Information Transfer. *J. Am. Chem. Soc.* **120,** 9810–9817 (1998).

62. Sato, T. *et al.* Polyisocyanates and the Interplay of Experiment and Theory in the Formation of Lyotropic Cholesteric States. *Macromolecules* **25,** 4551 (1992).

63. Tang, K., Green, M. M., Cheon, K. S., Selinger, J. V. & Garetz, B. A. Chiral conflict. The effect of temperature on the helical sense of a polymer controlled by the competition between structurally different enantiomers: From dilute solution to the lyotropic liquid crystal state. *J. Am. Chem. Soc.* **125,** 7313–7323 (2003).

64. Zheng, Z. *et al.* Three-dimensional control of the helical axis of a chiral nematic liquid crystal by light. *Nature* **531,** 352–356 (2016).

65. Eelkema, R. *et al.* Molecular machines: nanomotor rotates microscale objects. *Nature* **440,** 163 (2006).

66. Iamsaard, S. *et al.* Conversion of light into macroscopic helical motion. *Nat. Chem.* **6,** 229–235 (2014).

67. Aßhoff, S. J. *et al.* High-Power Actuation from Molecular Photoswitches in Enantiomerically Paired Soft Springs. *Angew. Chem. Int. Ed.* (2017). doi:10.1002/anie.201611325

68. Katsonis, N., Lacaze, E. & Feringa, B. L. Molecular chirality at fluid/solid interfaces: expression of asymmetry in self-organised monolayers. *J. Mater. Chem.* **18,** 2065–2073 (2008).

69. Parschau, M. & Ernst, K.-H. Disappearing Enantiomorphs: Single Handedness in Racemate Crystals. *Angew. Chemie Int. Ed.* **54,** 14422–14426 (2015).

70. Sakaguchi, H., Song, S., Kojima, T. & Nakae, T. Homochiral polymerization-driven selective growth of graphene nanoribbons. *Nat. Chem.* **9,** 57–63 (2017).

71. Masini, F. *et al.* Chiral induction by seeding surface assemblies of chiral switches. *J. Am. Chem. Soc.* **133,** 13910–13913 (2011).

72. Parschau, M., Romer, S. & Ernst, K.-H. Induction of homochirality in achiral enantiomorphous monolayers. *J. Am. Chem. Soc.* **126,** 15398–15399 (2004).

73. Fang, Y. *et al.* Dynamic control over supramolecular handedness by selecting chiral induction pathways at the solution–solid interface. *Nat. Chem.* **8,** 711–717 (2016).

74. Fasel, R., Parschau, M. & Ernst, K. H. Amplification of chirality in two-dimensional enantiomorphous lattices. *Nature* **439,** 449–452 (2006).

75. Yun, Y. J. & Gellman, A. J. Adsorption-induced auto-amplification of enantiomeric excess on an achiral surface. *Nat. Chem.* **7,** 520–525 (2015).

76. Ortega Lorenzo, M., Baddeley, C. J., Muryn, C. & Raval, R. Extended surface chirality from supramolecular assemblies of adsorbed chiral molecules. *Nature* **404,** 376–379 (2000).

77. Lawton, T. J. *et al.* Long range chiral imprinting of Cu(110) by tartaric acid. *J. Phys. Chem. C* **117,** 22290–22297 (2013).

78. Orme, C. a *et al.* Formation of chiral morphologies through selective binding of amino acids to calcite surface steps. *Nature* **411,** 775–779 (2001).

79. Roth, C., Parschau, M. & Ernst, K. H. Chiral reconstruction of a metal surface by adsorption of racemic malic acid. *ChemPhysChem* **12,** 1572–1577 (2011).

80. Gellman, A. J. *et al.* Superenantioselective Chiral Surface Explosions. *J. Am. Chem. Soc.* **135,** 19208–19214 (2013).

81. Lieberman, I., Shemer, G., Fried, T., Kosower, E. M. & Markovich, G. Plasmon-Resonance-Enhanced Absorption and Circular Dichroism. *Angew. Chemie Int. Ed.* **47,** 4855–4857 (2008).

82. Srivastava, S. *et al.* Light-Controlled Self-Assembly of Semiconductor Nanoparticles into Twisted Ribbons. *Science* **327,** 1355–1359 (2010).

83. Zhou, Y. *et al.* Biomimetic Hierarchical Assembly of Helical Supraparticles from Chiral Nanoparticles. *ACS Nano* **10,** 3248–3256 (2016).

84. Vázquez-Nakagawa, M., Rodríguez-Pérez, L., Herranz, M. A. & Martín, N. Chirality transfer from graphene quantum dots. *Chem. Commun.* **52,** 665–8 (2015).

85. Suzuki, N. *et al.* Chiral Graphene Quantum Dots. *ACS Nano* **10,** 1744–55 (2016).

86. Govorov, A. O. *et al.* Chiral nanoparticle assemblies: circular dichroism, plasmonic interactions, and exciton effects. *J. Mater. Chem.* **21,** 16806 (2011).

87. Dolamic, I., Varnholt, B. & Bürgi, T. Chirality transfer from gold nanocluster to adsorbate evidenced by vibrational circular dichroism. *Nat. Commun.* **6,** 7117 (2015).

88. Jin, R. Atomically precise metal nanoclusters: stable sizes and optical properties. *Nanoscale* **7,** 1549–65 (2015).

89. Ben-Moshe, A., Govorov, A. O. & Markovich, G. Enantioselective Synthesis of Intrinsically Chiral Mercury Sulfide Nanocrystals. *Angew. Chemie Int. Ed.* **52,** 1275–1279 (2013).

90. Singh, G. *et al.* Self-assembly of magnetite nanocubes into helical superstructures. *Science* **345,** (2014).

91. Grzelczak, M., Vermant, J., Furst, E. M. & Liz-Marzán, L. M. Directed Self-Assembly of Nanoparticles. *ACS Nano* **4,** 3591–3605 (2010).

92. Guerrero-Martínez, A. *et al.* Intense Optical Activity from Three-Dimensional Chiral Ordering of Plasmonic Nanoantennas. *Angew. Chemie Int. Ed.* **50,** 5499–5503 (2011).

93. Wang, R.-Y. *et al.* Chiral assembly of gold nanorods with collective plasmonic circular dichroism response. *Soft Matter* **7,** 8370–8375 (2011).

94. Mitov, M., Portet, C., Bourgerette, C., Snoeck, E. & Verelst, M. Long-range structuring of nanoparticles by mimicry of a cholesteric liquid crystal. *Nat. Mater.* **1,** 229–231 (2002).

95. Querejeta-Fernández, A., Chauve, G., Methot, M., Bouchard, J. & Kumacheva, E. Chiral plasmonic films formed by gold nanorods and cellulose nanocrystals. *J. Am. Chem. Soc.* **136,** 4788–4793 (2014).

96. Kuzyk, A. *et al.* DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response. *Nature* **483,** 311–314 (2012).

97. Yan, W. *et al.* Self-assembly of chiral nanoparticle pyramids with strong R/S optical activity. *J. Am. Chem. Soc.* **134,** 15114–15121 (2012).

98. George, J. & Thomas, K. G. Surface Plasmon Coupled Circular Dichroism of Au Nanoparticles on Peptide Nanotubes. *J. Am. Chem. Soc.* **132,** 2502–2503 (2010).

99. Chen, W. *et al.* Nanoparticle superstructures made by polymerase chain reaction: Collective interactions of nanoparticles and a new principle for chiral materials. *Nano Lett.* **9,** 2153–2159 (2009).

100. Molotsky, T., Tamarin, T., Moshe, A. Ben, Markovich, G. & Kotlyar, A. B. Synthesis of Chiral Silver Clusters on a DNA Template. *J. Phys. Chem. C* **114,** 15951–15954 (2010).

101. Merg, A. D. *et al.* Peptide-Directed Assembly of Single-Helical Gold Nanoparticle Superstructures Exhibiting Intense Chiroptical Activity. *J. Am. Chem. Soc.* **138,** 13655–13663 (2016).

102. Shen, X. *et al.* Rolling up gold nanoparticle-dressed dna origami into three-dimensional plasmonic chiral nanostructures. *J. Am. Chem. Soc.* **134,** 146–149 (2012).

103. Lan, X. *et al.* Au nanorod helical superstructures with designed chirality. *J. Am. Chem. Soc.* **137,** 457–462 (2015).

104. Shen, X. *et al.* Three-dimensional plasmonic chiral tetramers assembled by DNA origami. *Nano Lett.* **13,** 2128–2133 (2013).

105. Mastroianni, A. J., Claridge, S. & Alivisatos, A. P. Pyramidal and Chiral Grouping of Gold Nanocrystals Assembled Using DNA Scaffolds. *J. Am. Chem. Soc.* **131,** 8455–8459 (2010).

106. Wu, X. *et al.* Propeller-Like Nanorod-Upconversion Nanoparticle Assemblies with Intense Chiroptical Activity and Luminescence Enhancement in Aqueous Phase. *Adv. Mater.* **28,** 5907–5915 (2016).

107. Wu, X. *et al.* Unexpected chirality of nanoparticle dimers and ultrasensitive chiroplasmonic bioanalysis. *J. Am. Chem. Soc.* **135,** 18629–18636 (2013).

108. Shopsowitz, K. E., Qi, H., Hamad, W. Y. & MacLachlan, M. J. Free-standing mesoporous silica films with tunable chiral nematic structures. *Nature* **468,** 422–425 (2010).

109. Qi, H., Shopsowitz, K. E., Hamad, W. Y. & MacLachlan, M. J. Chiral nematic assemblies of silver nanoparticles in mesoporous silica thin films. *J. Am. Chem. Soc.* **133,** 3728–3731 (2011).

110. Yeom, J. *et al.* Chiral templating of self-assembling nanostructures by circularly polarized light. *Nat. Mater.* **14,** 66–72 (2015).

111. Kim, Y. *et al.* Reconfigurable chiroptical nanocomposites with chirality transfer from the macro- to the nanoscale. *Nat. Mater.* **15,** 461–468 (2016).

112. Di Mauro, A. *et al.* Vortexes tune the chirality of graphene oxide and its non-covalent hosts. *Chem. Commun.* **52,** 13094–13096 (2016).

113. Kuzyk, A. *et al.* A light-driven three-dimensional plasmonic nanosystem that translates molecular motion into reversible chiroptical function. *Nat. Commun.* **7,** 10591 (2016).

114. Kuzyk, A. *et al.* Reconfigurable 3D plasmonic metamolecules. *Nat. Mater.* **13,** 862–866 (2014).

115. Fenniri, H. *et al.* Entropically driven self-assembly of multichannel rosette nanotubes. *Proc. Natl. Acad. Sci. U. S. A.* **99,** 6487–6492 (2002).

116. Motojima, S. & Chen, Q. Three-dimensional growth mechanism of cosmo-mimetic carbon microcoils obtained by chemical vapor deposition. *J. Appl. Phys.* **85,** 3919–3921 (1999).

117. Sharma, V., Crne, M., Park, J. O. & Srinivasarao, M. Structural Origin of Circularly Polarized Iridescence in Jeweled Beetles. *Science* **325,** 449–452 (2009).

Figure legends

Figure 1 Types of chirality. a) Molecular or local chirality: cysteine features a carbon centre with four different attached groups. **b)** Axial or helical chirality where molecules are chiral by restricted rotation about an axis. **c)** Supramolecular structures or polymeric assemblies may also be chiral. Illustrated here is the formation of helical rosette nanotubes, from achiral monomers,[115] and a DNA helix**. d)** Macroscopic chirality in plant tendrils and carbon microcoils.[116] **e-f)** Diastereomeric interactions: two enantiomers are energetically equivalent in an achiral environment, as illustrated by the enantiomeric pairs of a tetrahedron and a helix (**e** and **f**). In a chiral environment, represented by reaction with a chiral species above the arrow, the two enantiomers are no longer equivalent. The interaction produces diastereomers which have different energies, and different chemical and physical properties. **g)** A 50:50 mixture of two helices may form different aggregates which are diastereotopic and different in energy. Represented is a lower energy conglomerate (right), which preferentially forms two homochiral domains (like species preferentially interact) over heterochiral domains (left, where enantiomeric pairs form). The opposite preference (heterochiral over homochiral) may also be observed and which (if either) is favoured will depend on the chemical system.

Figure 2 Mechanisms of transmission. a) Amplification of chirality: polyisocynates preferentially adopt helical conformations in solution. The handedness of the helix can be biased by the introduction of a chiral element in the monomers, as shown here with deuterium substitution.[29] Meijer and co-workers have established a similar effect in supramolecular helices made up of stacked chiral monomers, though the effect is weaker than in the covalent case.[30] **b)** “Sergeants and Soldiers” and “Majority Rules” effects can dictate the overall supramolecular conformation of helical structures, and these same concepts are useful in non-covalent systems, liquid crystals, on surfaces, and in larger three-dimensional structures. **c)** Transmission of chiral information through space: in an oligomer composed of achiral building blocks, chiral residues at the helix terminus induce diastereoselectivity in a reaction about 4 nm away.[48] **d)** A molecular motor at the terminus of a polyisocyanate chain can selectively control helix handedness by switching states.[54]

Figure 3 Transmission in ordered assemblies. a) In the nematic phase of a liquid crystal all molecules are aligned along a director. In a chiral nematic phase there is an additional degree of ordering by a helical twist along an axis perpendicular to the director. **b)** Helical deformations: Katsonis and co-workers demonstrated that a polymeric chiral liquid crystal network cut at different angles gave various helical ribbons. The network incorporates azobenzene photo-switches, which upon irradiation disturb the LC structure and cause macroscopic deformations of the helices.[66] **c)** Majority rules on a surface: Chiral helicene molecules pack into enantiomorphous domains (red and yellow domains, λ and ρ). The use of scalemic helicene results in a strong chiral amplification, where the major enantiomer dictates which enantiomorphous domain is adopted and transmits this preference across the whole surface.[74]

Figure 4 Transmission of chirality in nanomaterials: a) Nanocrystalline cellulose (NCC) displays chiral nematic ordering with a helical half pitch P/2 of ~ 150 – 650 nm. A polarised optical microscopy image of its suspension with a silica precursor shows macroscopic helical chirality, templated from the NCC.[108] The solid state chiral nematic ordering of chitin is responsible for the iridescence of beetle exoskeletons.[117] **b)** Macroscopic deformations: A mechanically induced twist in poly(dimethylsiloxane) before deposition of Au nanoparticles results in chiroptical activity, reflecting the twist, in the NP assembly.[111] **c)** Chiral nanoparticle assemblies: chirality may be expressed at the nanoparticle level *via* their assembly into chiral structures, commonly template by chiral macromolecules. Illustrated here are two prominent examples, arranging nanoparticles into helical or tetrahedral chiral shapes.[96,97] **d)** Circularly polarised light directs nanoparticle assembly: nanoparticles rendered chiral by their truncated tetrahedral shape show different efficiency for the absorption of circularly polarised light. One handedness of the nanoparticles is therefore preferentially photooxidised and undergoes a subsequent self-assembly to a single handed helical ribbon.[110]