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# Materials for chiral light control

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**Solution-processable semiconductors based on small molecules, polymers or halide perovskites combine sustainable manufacturing with exceptional optoelectronic properties that can be chemically tailored to achieve flexible and highly efficient optoelectronic and photonic devices. A new exciting research direction is the study of the influence of chirality on light–matter interactions in these soft materials and its exploitation for the simultaneous control of charge, spin and light. In this Viewpoint, researchers working on different types of chiral semiconductors discuss the most interesting directions in this rapidly expanding field.**

## Chirality in helical semiconducting molecules

**Jeanne Crassous:** Light-emitting chiral molecules may exhibit circularly polarized luminescence (CPL). This fascinating property, first discovered in 1948 in a chiral crystal of sodium uranyl acetate, $Na[UO_2(CH_3COO)_3]$, has received growing attention owing to three advances: the development of CPL spectroscopy between the 1960s and the 1980s, the subsequent commercialization of CPL apparatuses operating from the ultraviolet to the infrared (IR) domain and the opportunity to use chiral molecules in optoelectronics, spintronics and biology (Fig. 1). CP light is used in CP organic light-emitting diodes (OLEDs), spin LEDs (as discussed in the contribution of Matthew Beard), lighting and 3D displays. It can also be used to code the light in anti-counterfeiting systems and to deliver high sensitivity in CP bioimaging and detection. Optical components such as linear polarizers and quarter-wave plates are used in devices to generate polarized light and to eliminate glare. However, they cut part of the light and may thus be advantageously replaced by chiral CPL emitters.

A strong chiroptical activity, that is, an intense differential response between left-handed and right-handed CP light, is desired both in absorption (circular dichroism) and in emission (CPL). The chiroptical activity can be quantified by the dissymmetry (or $g$) factor, which is defined as:

$$g = \frac{I_{LH} - I_{RH}}{1/2(I_{LH} + I_{RH})}, \quad (1)$$

where $I_{LH}$ and $I_{RH}$ are the left-handed and right-handed absorption/emission intensities, respectively. An ideal system would produce maximum $g$-values of −2 and +2 upon emission of pure right-handed or left-handed polarized light, respectively, after standard excitation, but many chiral fluorescent and phosphorescent molecules exhibiting CPL display $g$-values in the range of $10^{-4}$–$10^{-1}$.

My group is currently working on helicenes, a special class of chiral organic semiconductors formed by $n$ *ortho*-fused aromatic rings. Owing to their helical topology combined with extended π-conjugation, they display strong chiroptical activity, and their optimization is an active research focus for chemists. In my group, we develop helicenic architectures to generate structural diversity, study the structure–CPL activity relationships and unveil rules and trends to enhance the CPL, and we work on incorporating these molecules into devices.

We have discovered that organic helicenes decorated with strongly interacting chromophores placed in appropriate positions yield enhanced CP fluorescence and that organic helicenic cores with H-bonding units may display CPL inversion upon aggregation[1]. We have also incorporated organometallic units such as platinacycles, iridacycles or rhenacycles into π-helical ligands and prepared helically chiral complexes with long-lived CP phosphorescence[2]. Through chemical engineering, we developed various helicenic ligands with classical coordinating units (such as phenylpyridine, bi-pyridine and $N$-heterocyclic carbenes). Our synthetic efforts are aimed at generating molecular architectures combining CPL activity with unusual properties such as chiral-induced spin selectivity (the so-called CISS effect) or magnetochirality[3], thus giving access to multifunctional chiral materials. Pure enantiomers can be obtained by chiral separation in high-performance liquid chromatography, and theoretical calculations rationalize how the metal or chromophore influences the photophysical and chiroptical properties of the π-helical core.

The $g$ factor is proportional to $(|m|/|\mu|)\cdot\cos\theta$, where $m$ and $\mu$ are, respectively, the magnetic and electric transition moments (from excited to fundamental states in emission) and $\theta$ is the angle between them. Hence, molecules with magnetically allowed and electrically forbidden transition moments with well-aligned directions are highly sought after. Exploiting this insight, we have developed molecular systems with improved performances that were successfully incorporated into CP-OLEDs[4].

Beyond helical chirality, the search for molecules for CP technologies is expanding to other types of chirality (which can be central, axial, planar or inherent to the molecule) and to achiral chromophores placed within a chiral environment. Introducing donor/acceptor units enables to tune the emission wavelength of the chiral emitters to reach challenging but technologically relevant spectral ranges, such as the deep-blue and IR domains.

A common issue is that at the molecular level, $g$-values are often limited to around 0.01–0.1 and that high brightness is also needed. To overcome these drawbacks, chemists are investigating several directions, including using appropriate physicochemical phenomena such as aggregation-induced emission, the formation of complexes between electron donors and electron acceptors (exciplex formation), triplet–triplet annihilation, thermally activated delayed fluorescence and the CISS effect and implementing chiral molecules into highly chiral media such as liquid crystals or chiral polymers (as discussed in the contribution of Matthew Fuchter). In general, it is important to remember that much care needs to be taken during CPL measurements of non-isotropic media because of potential artefacts.

Chiral molecular systems other than easily processable fully organic systems are also becoming available. For example, chiral lanthanide complexes provide extraordinary $g$-values of up to 1.4 owing to intraconfigurational $f \rightarrow f$ dipole transitions that are forbidden by electric transition dipole selection rules but allowed by magnetic transition dipole selection rules and have finely structured and highly tunable emission wavelengths. Replacing high-cost rare earths with cheap transition metals may be relevant for sustainability, and enantiopure $Cr^{III}$-based complexes with spin-flip emission recently showed $g$-values reaching 0.2.

Future attractive research directions include studying open-shell chiral systems to understand how the spin state or magnetic characteristics influence the emission properties and investigating other promising systems, which include, as discussed in other contributions in this Viewpoint, polymeric architectures, supramolecules, inorganic aggregates and hybrid perovskite systems with appealing energy transfers.

## The contributors

**Jeanne Crassous** is Director of Research at CNRS (Institut des Sciences Chimiques de Rennes, France). Her group develops heteroatomic and organometallic helicenes and chiral π-conjugated assemblies and examines their chiroptical (circular dichroism, circularly polarized luminescence), magnetic and spin-related (magnetochiral dichroism and chiral-induced spin selectivity effect) responses for optoelectronic and spintronic applications. She is also interested in fundamental aspects of chirality such as parity violation.

**Matthew J. Fuchter** is a Professor of Chemistry at Imperial College London. His group has broad research interests in the development of functional molecular systems for use in materials and medicine. One specific area of focus is the application of chirality to technologically relevant materials.

**Danna E. Freedman** is the F.G. Keyes Professor of Chemistry at MIT. Her laboratory's research focuses on applying inorganic chemistry to address challenges in physics. Specific examples include harnessing the atomistic control inherent in synthetic chemistry to create molecular units for quantum information science, and creating new magnetic materials by using pressures comparable to planetary cores.

**Nicholas A. Kotov** is the Irving Langmuir Distinguished University Professor in Chemical Sciences and Engineering and the Joseph B. and Florence V. Cejka Professor of Engineering at the University of Michigan. He is a pioneer of biomimetic nanostructures and self-assembled nanomaterials. Chiral nanostructures represent a focal point of his current work with translation to physics, chemistry, biology and medicine. Nicholas is a recipient of the ACS Award for Outstanding Achievements in Nanoscience, Newton Award (DOD), Turnbull Lectureship (MRS), Soft Matter and Biophysical Chemistry Award (RSC). Nicholas is a Fellow of the American Academy of Arts and Sciences and of the National Academy of Inventors. He is also an advocate for scientists with disabilities.

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**Matthew C. Beard** is a Senior Research Fellow at the National Renewable Energy Laboratory in Golden, CO, and Director of the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE). CHOISE studies the unique properties of hybrid semiconductors, including how chirality in the organic component can be utilized to control spin, charge and light in these hybrid systems. Matt's work was recognized with the DOE's E.O. Lawrence award and RSC Chemical Dynamics award.

**Sascha Feldmann** is a principal investigator and Rowland Fellow at Harvard University's Rowland Institute. His research aims to transform the way we produce and consume energy as a society. Towards this aim, his group studies novel soft semiconductors for spin-optoelectronic applications using ultrafast polarization-resolved spectroscopy.

### Chirality in organic conjugated polymers

**Matthew J. Fuchter:** Organic conjugated materials have revolutionized modern electronics, particularly display technologies. Reasons for their success include the ability to tune their optical behaviour via molecular design and synthesis and to fabricate ultrathin, conformable and low-power devices. In principle, when aiming to produce materials for chiroptical applications — applications that require the absorption and/or emission of CP light — organics should be good candidates. However, organic chromophores that operate via processes allowed by electric transition dipole selection rules have an important issue: the vast majority only have very weak chiroptical activity. The chiroptical activity can be quantified by the dissymmetry (or $g$) factor (Eq. 1), which has a maximal value of $|2|$. This useful metric can quantify the magnitude of chiroptical activity for various processes, from absorption and emission to electroluminescence in OLEDs and photocurrent in organic photodetectors. The $g$ factor of most organic chromophores is on the order of $10^{-3}$. When used to describe emission, this means that <1% of the generated light is CP. For most applications that use CP light, this value is simply nowhere near large enough.

To achieve large chiroptical activity in a chiral chromophore, it is critical to balance the magnitude and relative orientation of both the electric and magnetic transition dipoles. One approach is to use materials that use processes allowed by magnetic transition dipole selection rules, but forbidden by electric transition dipole selection rules. Unfortunately, such an approach is not particularly useful for electro-optical devices requiring CP luminescence, because the overall performance of the device is decreased. This leads to a well-established paradox: you can have either large chiroptical activity or efficient chromophores for absorption and/or emission, not both.

One class of organics that appears to overcome this paradox is conjugated polymers, particularly polyfluorenes. Since the late 1990s, it has been known that the attachment of chiral sidechains onto a polyfluorene backbone can give rise to polymer films with large chiroptical activity. In 2013, my collaborators and I pioneered an alternative approach, in which a chiral small-molecule additive is combined with a (non-chiral) polyfluorene in a blend film. The chiral small molecules induce a chiral structure into the polymer film, which, in turn, results in large chiroptical activity. Differences between the two approaches are still under investigation, but, to a first approximation, both provide a means to induce a large chiroptical activity. Indeed, we have now measured $g$ factors of ~1. When expressed in terms of emission, this means that the light generated is ~50% CP, which is a technologically relevant result. Using this material, we have prepared devices for CP light emission (CP-OLEDs) and CP light detection (CP-organic photodetectors), and our devices are currently the highest performing in this domain.

However, there are many remaining challenges. First, the precise mechanisms behind the large chiroptical activity of polyfluorene films remain elusive. It was traditionally thought that such materials act like a chiral nematic liquid crystalline material, resulting in a large apparent chiroptical activity as light propagates through the structurally chiral medium. We recently questioned this interpretation, with detailed comparative work suggesting instead that these polymer films have a large intrinsic chiroptical activity[5]. However, this result needs to be reconciled with the apparent paradox stated earlier. Further work on polyfluorene films points to the importance of exciton coupling between adjacent polymer chains and the need to include magnetic transition dipole terms within such exciton coupling, but further detailed structural and spectroscopic work is clearly needed. Only once a more complete understanding is developed can new materials with good chiroptical activity be rationally designed.

Second, the behaviour of such materials in devices requires detailed consideration and is subject to factors that counteract any intrinsic chiroptical activity. For example, for chiral emitters within a (transparent) host material in an OLED, light reflection within the device dramatically reduces the *g* factor. This is because CP light changes handedness upon reflection. Conversely, we have shown that light reflection within a CP planar heterojunction photodiode can enhance the *g* factor[6]. Most bizarrely, we have evidence that the handedness of the CP electroluminescence in chiral-emissive polyfluorene films is dependent not just on the handedness of the polymer but also on the direction of the electric current. We have tentatively assigned this effect to induced orbital angular momentum caused by the chiral polymeric medium[7], but there is clearly still much to be learnt in the physics of these intriguing materials.

## Molecular colour centres for quantum information science

**Danna E. Freedman:** Scientists and engineers across disciplines are harnessing our new-found control of quantum properties towards the broad range of fields encompassed by quantum information science. This nascent field focuses on the transition from the first quantum revolution, in which scientists observed the fundamental quantum nature of the universe, to the current second quantum revolution, quantum 2.0, wherein we are controlling quantum properties. Expanding from isolated quantum units towards complex systems requires quantum bits, or qubits, which are tuned for specific applications and environments. Designer qubits could enable transformative technologies, including fantastical-sounding notions such as the quantum internet, quantum computing and quantum metrology. Molecules are a prime candidate for designer quantum units. Their unique combination of atomic-scale tunability, reproducibility and chemical specificity makes paramagnetic molecules a paradigm-shifting category of materials. These properties have the potential to be transformative for developing a bespoke quantum ecosystem, as the requirements for a component of a quantum communications network are distinct and potentially orthogonal to those for a quantum sensor.

Thus far, molecules have demonstrated several key proof-of-concept features that are critical for the realization of quantum 2.0. Among those features are single-molecule readout, as elegantly demonstrated by electron spin resonance performed with a scanning tunnelling microscope, optical readout of spin information, execution of gate operations and realization of millisecond coherence times at low temperature. Moving from this foundation, molecules can now be tuned

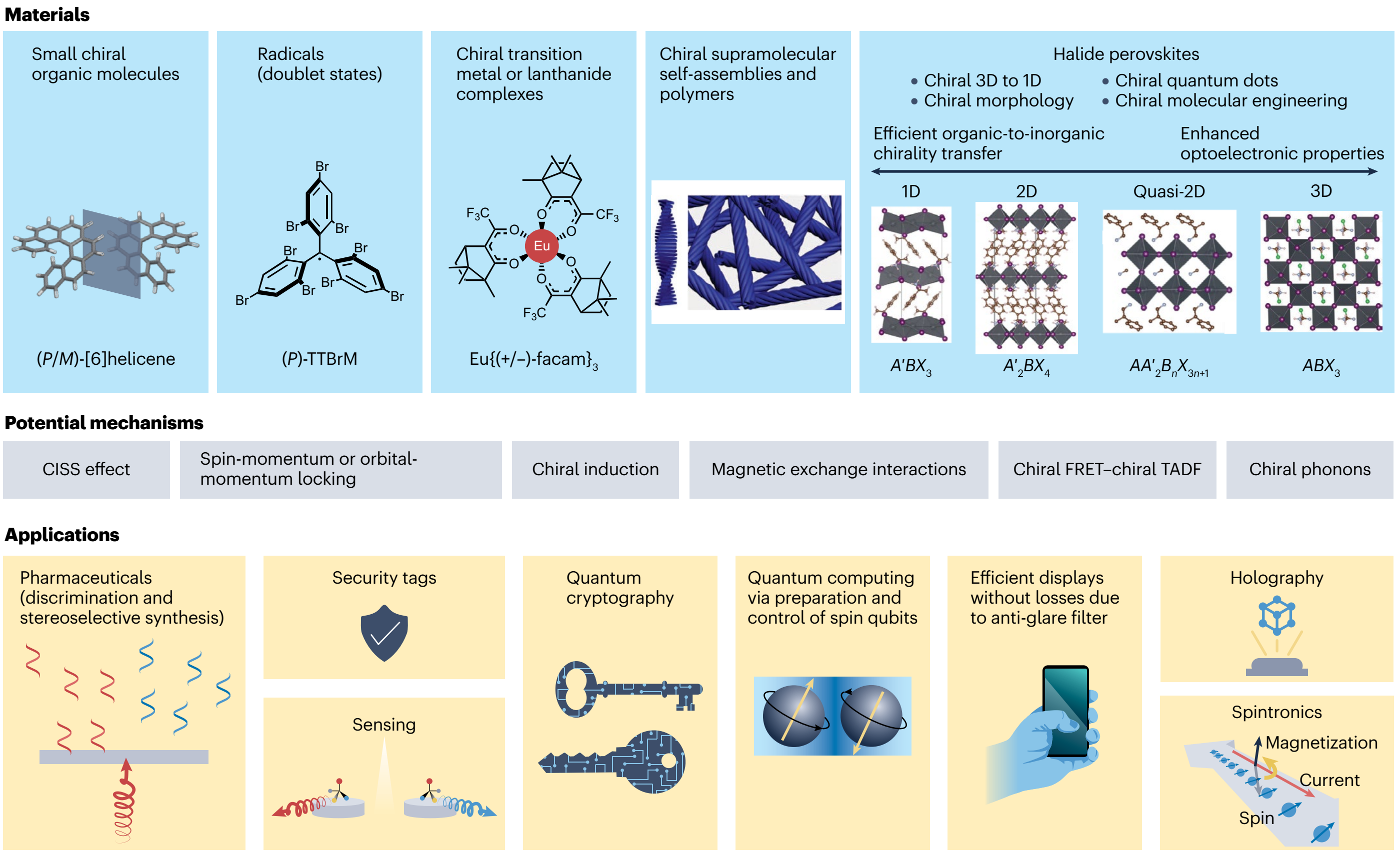

**Fig. 1 | Emerging semiconductors for chiral light control.** Overview of various promising chiral semiconducting materials (top), potential mechanisms (middle) and applications (bottom). *A*/*A′*, small/large cation; *B*, dication, for example, $Pb^{2+}$; CISS, chiral-induced spin selectivity; Eu{(+/−)-facam}$_3$, europium tris[3-(trifluoromethylhydroxymethylene)-(+/−)-camphorate]; FRET, Förster resonance energy transfer; TADF, thermally activated delayed fluorescence; TTBrM, tris(2,4,6-tribromophenyl)methyl radical; *X*, halide anion. Chiral supramolecular self-assemblies and polymers image adapted from ref. [21], CC BY 4.0. $A'BX_3$ image adapted from ref. [15], CC BY 4.0. $A'_2BX_4$ image adapted with permission from ref. [14], RSC. $AA'_2B_nX_{3n+1}$ image reprinted with permission from ref. [16], Wiley. $ABX_3$ image reprinted with permission from ref. [22], Wiley.

for specific environments and targeted towards specific applications within quantum information science.

For the purpose of this brief piece, I focus on using optical readout of spin information for quantum sensing. Sensing is inherently specific to an analyte and an environment. Optically addressable molecules, or 'molecular colour centres', offer a platform to integrate synthetic tunability with optical readout. One can imagine a new generation of custom-built sensors. For example, understanding local magnetic fields at and near surfaces is of interest to a large number of communities, such as those working on 2D magnets, skyrmions and twistronics. Integrating on-surface sensors that can be manipulated at angstrom-level distances could enable insight at the frontier of condensed matter physics. To create these systems, molecular colour centres would need to be surface-compatible and amenable to integration under low-temperature and high-vacuum conditions. This may require chemical tethering or integration with inert 2D materials such as hexagonal boron nitride (hBN). A separate class of applications for quantum sensors are within biological systems. An early target for molecular colour centres is integration with cryo-electron microscopy, in which spatial resolution could be complemented by magnetic insight from a quantum sensor. Molecules need to be imbued with biological compatibility, water solubility, for example, and they need to be compatible with readout at the higher but still relatively low temperatures intrinsic to cryo-electron microscopy measurements. Additionally, a critical feature of molecular colour centres is frequency tunability, thereby potentially enabling readout closer to the infrared portion of the spectrum. Molecules also offer an intriguing possibility of chiral readout. Specifically, chiral molecules are responsive to CP light. There is an elegant example of using CP light to polarize and readout Ce:YAG by exploiting a 4*f*-to-5*d* transition for CP-based spin polarization. Extending this idea to chiral molecules could be transformative for sensing because it would be a differentiable signal — the only species that would respond selectively to the CP light would be the sensor. This could be an efficient way to extract quantum signals through a messy chemical environment.

With the breadth of sensing applications, the unique tunability of molecules and the specificity of quantum sensing, molecules are a transformative tool for the next generation of quantum applications.

## Chiral phonons and terahertz circular dichroism

**Nicholas A. Kotov:** The development of terahertz circular dichroism spectroscopy opened a pathway to investigate mirror-asymmetric vibrational states with energies in the range 0.001–0.01 eV. Terahertz circular dichroism is essential, in particular, for the observation of complex motions of high-molecular-weight polymer segments with rotational components. One fascinating class of vibrations is represented by chiral phonons, which are long-range vibrations of multiple atoms and groups connected by primary and secondary chemical bonds that translate through the crystalline structure in a concerted helical motion[8].

Strong sensitivity of these helical vibrations to mirror asymmetries of the molecules and of the 'soft' chemical bonds makes them appealing for various applications that span biotechnology and medicine, such as quality control of pharmaceuticals and biomedical imaging. The diagnostic capabilities of these vibrational states were demonstrated by the observation of the evolution of chiral phonons in insulin nanofibrils as they assemble into fibres. In fact, nanoscale fibres of chiral materials are likely to show chiral phonon bands with enhanced intensity.

Both chiral and achiral solids can support the propagation of chiral phonons, which are observed both in nanoscale and in macroscale materials[9,10]. In stiff 2D materials, chiral phonons can also emerge at higher energies, in the IR part of the spectrum[9]. For example, 2D hexagonal lattices of $MoS_2$ and $WSe_2$ display spectroscopic signatures of chiral phonons between 0.5 and 2 eV (refs. [9–11]). Chiral phonons were observed in the corners of the Brillouin zone of these semiconductors using the valley phonon Hall effect[10]. Theoretical studies on other 2D platelet-like and sheet-like nanomaterials, such as $WN_2$, MoN and MoP, predict the presence of chiral phonons in these materials as well[12]. Note, however, that these hexagonal lattices are achiral. This is a big problem for these nanomaterials because one cannot resolve and utilize left-rotating and right-rotating phonons. By contrast, in $Co_3O_4$ nanoparticles with chiral distortions in the crystal lattice induced by chiral surface ligands, phonons with left and right helicity lose their degeneracy, such that Raman optical activity can distinguish them[13].

For the many biological materials interconnected by hydrogen bonds, which are 'softer' than covalent carbon–carbon or metal–sulfur bonds, terahertz circular dichroism spectroscopy is the perfect method to observe chiral phonons. Because most biological materials are chiral, the sign of the terahertz circular dichroism peaks uniquely corresponds to the helical motion of the propagating phonon. Furthermore, terahertz circular dichroism peaks for chiral phonons can be sharper than typical absorption peaks in the same range of energies because of the polarization narrowing typical of circular dichroism spectra and of the tight energy requirements imposed on chiral phonons by the collective nature of these vibrational states.

The ability to study chiral phonons in biomolecules has the potential to unlock insight into biochemical processes; hence, a pivotal finding was the observation of chiral phonons in crystalline amino acids[1], in which the sharpness of the bands is strongly correlated to the crystal symmetry. Unexpectedly, sharp terahertz circular dichroism and terahertz absorption peaks were observed for dispersions of microcrystals of His, Gln, Glu, Thr, Tyr and other amino acids; all these molecules crystalize in the $P2_12_12_1$ space group. Other amino acids, such as Phe, Met, Leu and Glu, that crystallize in other crystal lattices also have chiral phonon peaks, but they are broader. Serendipitously, the $P2_12_12_1$ space group is the most common one for chiral molecules; hence, chiral phonons can be observed for a wide range of biomolecules.

## Chirality in organic–inorganic hybrid perovskites

**Jooho Moon:** Since the first discovery of circular dichroism in chiral organic–inorganic hybrid perovskites (OIHPs) in 2017 (ref. [14]), chiral OIHPs have been regarded as a promising material platform for next-generation optoelectronic and energy-conversion devices owing to their unprecedented spin-related and chiroptical properties. Generally, chiral OIHPs adopt a low-dimensional layered structure with a chemical formula of $A'BX_3$ (in 1D) or $A'_2BX_4$ (in 2D), where $A'$ is a large-sized chiral organic cation, $B$ is a divalent metal cation and $X$ is a halide anion. Chiral OIHPs with various combinations of anions and cations can be developed through delicate material design, thus enabling the precise control of their chiroptical properties, such as circular dichroism, CP photoluminescence and CISS effect.

The chiroptical properties and polarization-based optical phenomena observed in chiral OIHPs can be explained as a function of chirality transfer from the $A'$-site chiral organic molecules to the achiral inorganic frameworks

($BX_3$ or $BX_4$). The intercalation of chiral organic molecules into the lattice of OIHPs can result in symmetry-breaking, thus facilitating the crystallization in a chiral space group. It is important to note that the chiroptical phenomena in chiral OIHPs are mainly associated with the first excitonic state of the inorganic framework, which is far from the excitonic state of chiral organic molecules. Therefore, the degree of chirality transfer (the degree of chiral lattice distortion induced in the inorganic frameworks) can be a critical factor for controlling the chiroptical activity of chiral OIHPs. From the crystal structure perspective, inorganic frameworks in chiral OIHPs exhibit two possible octahedron structures (face-sharing for 1D and corner-sharing for 2D) in the presence of A′-site chiral organic molecules. As the degree of lattice distortion and interaction between chiral organic molecules and inorganic frameworks vary with changes in the octahedron structure, dimensionality affects the chiroptical activity. One-dimensional chiral OIHPs exhibit a huge asymmetric chiroptical response, one order of magnitude higher than that of their 2D counterparts, because the 1D face-sharing inorganic octahedral is more sensitively affected by the helicity of the chiral molecules. However, the low mobility and inferior carrier transport capability of low-dimensional chiral OIHPs, which result from their strong quantum confinement effect, hinder their practical application.

The chiroptical properties of chiral OIHPs can be controlled by carefully selecting the chiral organic molecules. Several chiral organic molecules have been adopted as the *A*′-site cation to demonstrate the effect of molecular structure on chirality transfer. Moreover, different structural isomers of chiral organic molecules, which have different molecular structures according to the location of the functional group, can be selected to enhance chirality transfer by delicately controlling intermolecular interactions (such as hydrogen bonding). The symmetry-breaking interaction between chiral molecules and inorganic frameworks can be further controlled by halogen substitution of the $\alpha$-methylbenzylammonium (MBA) cation ($X$-MBA, where $X$ = F, Br, Cl or I).

Tuning the composition of the inorganic frameworks ($BX_3$ or $BX_4$) can directly induce a change in the chiroptical properties of chiral OIHPs. First, the *B*-site metal divalent cation has a non-negligible impact on the spin-related and polarization-related properties owing to the strong spin–orbit coupling of heavy atoms in non-centrosymmetric systems. Several *B*-site metal cations, such as Sn, Cu, Ag and Bi, have been used to achieve extraordinary optical and spin-related properties. In addition, halide composition engineering, which affects the electronic band structure of chiral OIHPs, could be an effective strategy to tune the chiroptical response of chiral OHIPs over a broad wavelength range.

Owing to their intrinsic chiroptical properties and outstanding optoelectronic properties, chiral OIHPs have attracted considerable research attention as a polarization-sensing material. Recently, an OIHP-based CP light photodetector has been reported[15]. The photodetector based on 1D or 2D chiral OIHPs can be optimized using either a chiral organic substitution strategy or a dimension control strategy. However, low-dimensional chiral OIHPs have the intrinsic limitation of displaying a multi-quantum-well structure, resulting in CP light photodetectors with inferior responsivities. To address this issue, a CP light photodetector based on quasi-2D chiral OIHPs with an increased average number of inorganic layers has been developed, obtaining a high responsivity of 1.1 A $W^{-1}$ (ref. [16]). However, an increase in the number of layers inevitably deteriorates the chiroptical response owing to a low degree of chirality transfer in inorganic frameworks. Several strategies can be used to resolve this paradox, including the modification of the dielectric constant by halogen substitution, strain engineering or utilization of the Dion–Jacobson phase without van der Waals gaps between adjacent cations. The intercalation of guest molecules into the lattice of chiral OIHPs, such as crosslinkable chiral cations with vinyl groups and Lewis bases with high electron donating ability, could also become a viable strategy to simultaneously enhance the chiroptical response and responsivity of CP light photodetectors.

## Chirality in hybrid metal–halide semiconductors for spin-LEDs

**Matthew C. Beard:** The ability to simultaneously control charge, spin and light at room temperature is highly desirable for many electro-optic applications, including spin-polarized LEDs (spin-LEDs). In spin-LEDs, CP light is emitted when spin-polarized carriers radiatively recombine. To fabricate a spin-LED, two components are needed: spin-polarized carriers and an emitter layer that emits CP light when injected with those polarized carriers. The polarization efficiency is a product of the spin-polarized current, spin-injection and polarized emission efficiency. Typically, spin currents are produced from ferromagnets or ferromagnetic semiconductors and/or in the presence of an applied magnetic field. Spin-LEDs are normally fabricated by injecting spin-polarized current into a III–V semiconductor light emitter. CP light must be emitted before a spin-flip that randomizes the spin polarization: low temperatures can help by suppressing spin-scattering channels but are inconvenient for practical applications.

Spin can also be controlled through the CISS effect: because in an oriented chiral medium, the movement of charges depends on their spin configuration, such systems can be used to control spin populations without magnetic components. The CISS effect was discovered by Ron Naaman and Dave Waldeck about 20 years ago, but mainly studied in oriented chiral organic molecules and their assemblies. A few years ago, CISS was discovered in a hybrid organic–inorganic semiconductor[17,18], a system that can also control charge and light and that can be solution-deposited on various platforms and integrated into devices, including spin-LEDs.

Hybrid metal–halide systems comprise organic and inorganic interpenetrating sublattices and exhibit properties that arise from both components, as well as unique emergent properties that result from the interaction of the inorganic and organic components. When the organic component consists of chiral molecules, the resulting hybrid structure is also chiral, resulting in a unique family of chiral hybrid semiconductors. Importantly, pure enantiomeric pairs can be readily prepared, that is, the enantiomeric purity is determined by the purity of the organic building blocks. Depending on the choice of the inorganic and organic components, various structural motifs have been observed, ranging from 0D isolated metal–halide subunits interspersed in a chiral organic matrix to 2D and quasi-2D metal–halide sheets with various metal–halide connectivity motifs that are separated by chiral organic layers[19]. The metal can range from $Pb^{2+}$ and $Sn^{+2}$, that is, group IV metals, to transition metals, including magnetic elements such as Cu, Fe and Cr. Mixed metal compounds have also been explored, and the range of systems that could be achieved by combining different metals with chiral organic amines is much larger than the number of systems that have been synthesized and characterized so far.

A unique advantage of these chiral semiconductors is that they can be cast as highly crystalline and textured thin films, with the 2D metal–halide planes oriented parallel to the substrate and the organic molecules oriented perpendicular to it. The films are highly uniform with a low degree of surface roughness and thickness easily tunable from tens to hundreds of nanometres. These properties make these films good candidates for integration into platforms that can be used to control charge, spin and light. Because semiconductors are non-magnetic systems that allow for the control of charge transport and for the absorption and emission of light, introducing chirality enables control over charge, spin and light without the need for magnetic components. Reports of the CISS effect in chiral metal–halide semiconductors have resulted in breakthroughs in the understanding of the effect and in the realization of spin-dependent optoelectronic properties.

CISS-enabled spin-LEDs have been demonstrated using a chiral metal–halide layer — 2D chiral $(MBA)_2PbI_4$ — paired with a non-chiral, light-emitting metal–halide layer[20]. The chiral layer transports and spin-polarizes holes before injecting them in the non-chiral layer, where they radiatively recombine with electrons, injected from the other contact, with the appropriate spin orientation. The resulting light polarization is fully determined by the handedness of the chiral semiconductor. This spin-LED operates at room temperature without any magnetic field or ferromagnetic contact. The polarized emission efficiency is determined by the spin scattering in the emitter layer rather than by the spin-polarized current or spin injection, thus improvements in the spin scattering should enhance the chiral-light polarization.

CP electro-luminescence generated at room temperature without external magnetic fields or ferromagnetic metals has potential applications in future 3D displays, holograms and virtual, augmented and extended reality, as well as in other technologies using chiral light, such as spin-lasers. Spin-LEDs have some advantages over other sources of chiral light. The emission colour can be readily tuned by changing the composition and size of the metal–halide perovskite nanocrystal emitters. The emitters themselves have narrow emission linewidth (full width at half maximum <20 nm), wide colour gamut and high photoluminescence efficiency. Finally, the spin orientation of the injected carriers can be modulated using two contacts of different chiralities or placing layers with opposite handedness close to one another, for example, in a display technology.

Beyond spin-LEDs, the use of chiral metal–halide semiconductors for controlling spins, charge and light has great potential in applications such as bio-encoding, information technologies and opto-spintronics.

## Ultrafast spectroscopy of chiral semiconductors

**Sascha Feldmann:** What all the different soft semiconductors discussed so far have in common is their ability to leverage permanent or temporarily-induced chirality in the excited state to generate CP light. What is still not well understood is exactly how structural chirality becomes imprinted onto the electronic states, for example, for chiral molecules or halide perovskites that contain chiral molecules, and what design principles ultimately yield a high degree of polarization, measured typically as a high emission dissymmetry factor.

For example, does the fact that the emission intensity is proportional to the scalar product of the electronic and magnetic dipole transition moment imply that no single material can ultimately combine a high radiative rate with an equally high CP emission, or could there be a dynamic non-equilibrium state formed for a chiral transition that, when stimulated to emit, leads to a large dissymmetry factor? And could couplings of electronic and magnetic quadrupole moments be leveraged for such purposes as well? To truly understand the mechanism behind the emergence of chiral information in the excited state, ultrafast time-resolved optical spectroscopy covering femtosecond to nanosecond timescales while simultaneously controlling and reading out the polarization of the excitation, probe and emission beams, will be essential.

Transient polarization-resolved measurements also allow for the investigation of recently observed chirality transfer systems, in which the chiral information of a chiral soft semiconductor seems to be transferred onto an emissive non-chiral acceptor, for example, from a small chiral molecule to an achiral polymer, or from a chiral perovskite layer to an achiral one. In these cases, the transient polarization of the initial state and of the subsequently generated excited states needs to be tracked in time to understand the role that Förster and Dexter-like energy transfer or even chiral phonons may play in invoking chirality in the electronic state beyond purely structural static chiral induction.

A related important question is what is the role of the electron spin in the manipulation of chiral light. Spin-polarized currents have long been known to induce CP emission in LEDs upon carrier recombination of the polarized charges. However, the recently reported CISS effect implies that such spin-polarized currents can also be achieved in the absence of ferromagnetic contacts and externally applied magnetic fields, even at room temperature, and be simply induced by charges moving through a chiral material. It has been proposed that such chiral structures act as spin filters via the coupling of the velocity of electron to the chiral electrical potential generated by the atomic nuclei and via the interaction of the resulting effective magnetic field with the magnetic moment of the electron given by its spin. The exact mechanism underlying recent spin-filter observations is under debate, and to elucidate it transient measurements, rather than the static measurements reported to date, need to be performed, both for optical polarization and for electric (spin-)current measurements. Ideally, such measurements should have sufficient spatial resolution to track spins in space as well as in time, as charges seemingly become polarized while they propagate across the chiral material, but may also become depolarized owing to structural disorder in films, or be subject to spin-momentum or orbital-momentum locking.

The CISS effect is typically used as a model for describing single-electron phenomena, for example, for chiral radical molecules or in the description of spin-polarized charge currents, but is rarely considered for the spin multiplicity of multi-electron states. Molecular triplet excitons, or in fact quartet and even quintet states, whose role is being investigated in phenomena such as singlet fission or triplet fusion, could also be strongly affected by the chirality of the involved structures. It will be crucial to understand whether chiral light harvesting can occur, for example, through chiral triplet–triplet annihilation up-conversion involving chiral annihilators and achiral bright singlet emitters, or vice versa. This way, the electronic and magnetic dipole moment limitations could be effectively overcome, perhaps within a single molecule or material. Similarly, studying the impact of spin–orbit coupling, ranging from weak (as in chiral small molecules and certain transition-metal complex qubit candidates) to strong (such as in chiral halide perovskites), on chirality transfer and coherence times will be extremely insightful.

Ultimately, spectroscopy resolved in time, energy and polarization, and performed under variable temperatures and magnetic fields, will be key to unravelling the mechanism behind chiral information transfer from a symmetry-broken structure to the electronic state, and to achieving full control of chiral excited states. These advances will pave the way for the optical preparation and readout of polarization states with the high fidelity needed to enter the age of quantum information processing powered by chiral systems tailored through chemical design.

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## Competing interests

D.E.F. has a patent filed on molecular colour centres. M.J.F. is an inventor on a patent concerning chiral blend materials (WO2014016611). M.C.B. has a patent filed related to CISS enabled spin-LEDs. The other authors declare no competing interests.

## Additional information