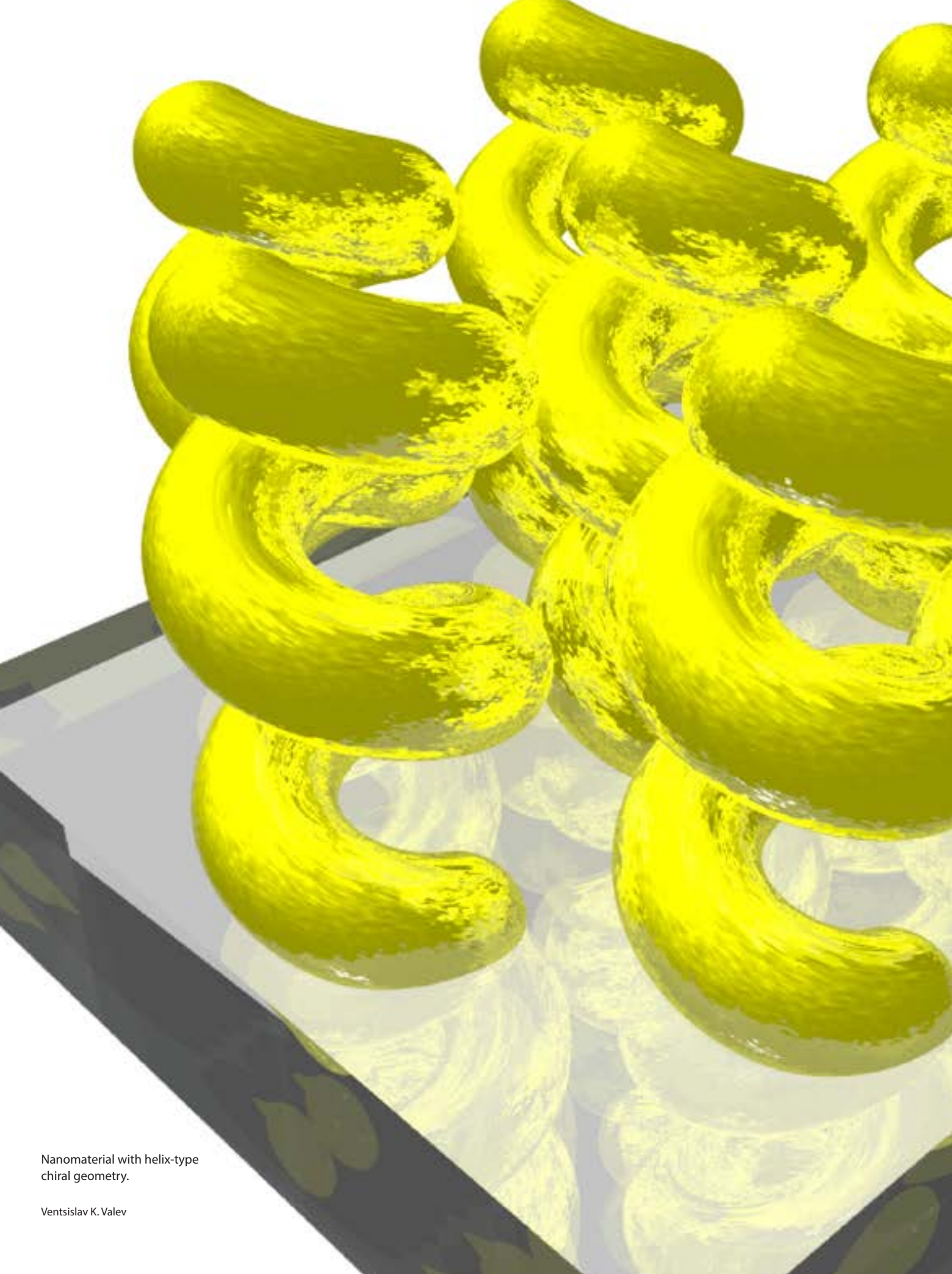
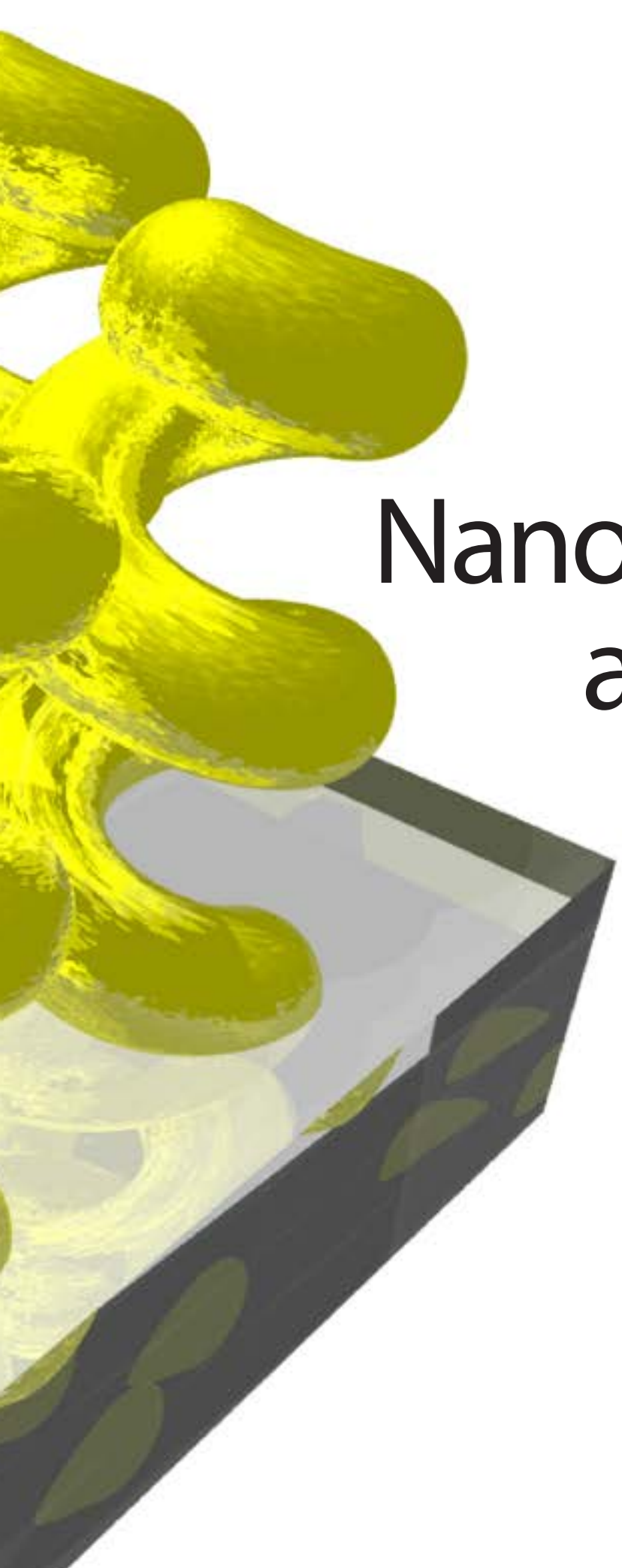


Nanomaterial with helix-type chiral geometry.

Ventsislav K. Valev



Ventsislav K. Valev

Chiral Nanomaterials and Chiral Light

Advances in nanofabrication are expanding opportunities to exploit and customize the "handedness" of materials—and of light itself.

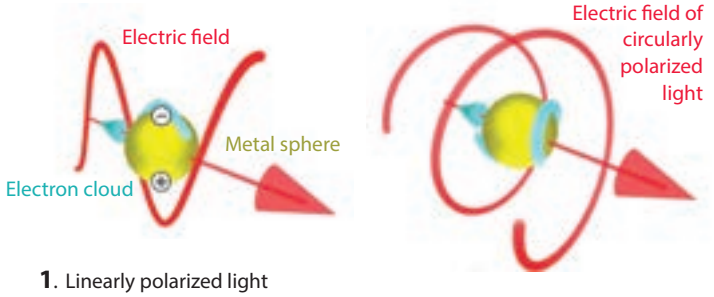
From spiral galaxies and hurricanes to seashells and amino acids, natural systems exhibit a sense of twist known as chirality (from the Greek *cheir*, meaning "hand"). A pair of chiral objects constitute mirror images that cannot be superimposed on each other, like the left and right hand—and, indeed, an object is said to have left-handed or right-handed chirality, depending on its sense of twist.

Biological objects such as seashells commonly exhibit only a single "handedness" in nature—as do their building blocks. For instance, all functional amino acids are left-handed, whereas all sugars (including the ribose that forms the backbone of DNA) are right-handed. Just as the standardized right-handed screw allows for efficient manufacturing, the single handedness of life's molecular building blocks allows for an efficient biochemistry—often with significant consequences. It is differences in molecular chirality, for example, that account for the difference in the scent of an orange and a lemon. And, in the pharmaceutical industry, distinguishing molecular chirality can be a matter of life and death.

Circularly polarized light has its own sense of twist—and it was through such chiral light that molecular chirality was discovered in the first place. Ever since, light has been used to identify the chirality of molecules. But although intensely studied for most of the last century, progress in chiral light-matter interaction has been hampered by a relative inability to manipulate material design parameters such as the length and orientation of chemical bonds. Moreover, because of the large discrepancy between the wavelength of light and the scale of chirality in small molecules (a few nm), light usually interacts only weakly with chiral molecules.

Recently, new techniques in nanofabrication and design have bridged this gap in dimensions, giving rise to chiral nanomaterials. These emerging materials are creating new opportunities both for demonstrating exotic optical effects, such as negative refractive indices, and for dramatically increasing chiral-optical (chiroptical) interactions between light and matter. These interactions, in turn, could expand the use of light for chiral sensing, chiral separation and chiral synthesis—all vital functions for modern biochemistry and pharmaceuticals.

Light-matter coupling in chiral nanomaterials



1. Linearly polarized light causes localized resonant plasmon oscillations at the surface of a metal nanosphere.

2. For circularly polarized light the surface plasmons follow a helix.

3. A chiral nanoparticle's shape can accommodate the plasmonic helix generated by CPL, yielding strong chiroptical interaction.

4. An unphysical mismatch between the shape of the nanostructure and the ideal plasmonic helix, by contrast, yields a weak chiroptical interaction.

Understanding chiral light-matter interactions

The elementary units of chiral nanomaterials are typically between a few and several hundred nanometers in size. This range allows them to bridge the gap between the length at which chirality is expressed in small molecules (on the lower end of the scale) and the wavelengths of light. Crucial to creating that bridge are metal nanostructures that can support surface plasmon resonances (SPRs)—coherent electron oscillations that can take place at metal/dielectric interfaces. When excited by light, SPRs have the same frequency as the incident light, but a shorter wavelength. This behavior allows light to be effectively "squeezed" towards shorter length scales, yielding efficient coupling with the

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For chiral metal nanostructures, a surface plasmon resonance couples preferentially to one direction of CPL—a key observation for understanding chiroptical effects.

geometry of the metal nanostructures and increasing the light-matter interaction with molecules.

We can gain insight on this plasmonic behavior by considering light incident on a metal sphere. For an excitation with linearly polarized light, the free electrons at the surface can be described as a simple harmonic oscillator, which resonates for a certain frequency of light that depends on the size of the nanoparticle, the nature of the metal and the nature of the surrounding dielectric. At the resonant frequency, over several excitation cycles, the nanoparticle stores energy and increases the amplitude of its oscillating surface electric fields. The larger amplitudes yield an increase of the scattering cross section and, consequently, a frequency peak can be observed in the scattering spectra of such nanoparticles.

Linearly polarized light can be thought of as a superposition of left- and right-hand circularly polarized light (CPL). CPL is chiral, since the electric field describes a helix of a single handedness along the propagation direction. Thus, CPL incident on the metal nanosphere causes a counterpropagating "plasmonic helix." Because the nanoparticle is spherical, the opposite CPL causes the opposite plasmonic helix.

For linearly polarized light, the two opposite plasmonic helixes cancel. However, if the nanoparticle is itself chiral (rather than symmetrical like a sphere), then, depending on its handedness, the plasmonic helix caused by CPL would either match the structure or not. As a result, for chiral metal nanostructures, a surface plasmon resonance will occur only for one direction of CPL—a key observation for understanding chiroptical effects.

Left and right, right and wrong

Chiral nanomaterials can enhance the interactions between light and chiral molecules, leading to improved chiral sensing and chiral separation. Being able to identify and separate left- from right-handed molecules is extremely important for chemistry, biochemistry and pharmaceutical science.

Chirality's importance in life science was tragically demonstrated fifty years ago, when the drug thalidomide was prescribed to pregnant women to prevent morning sickness. The active molecule in the drug was chiral, and the drug itself was sold as a mixture of both chiral forms. One of those forms did indeed help with morning sickness—but its mirror image caused serious birth defects in more than 10,000 cases worldwide.

Since that experience, the molecules in chiral pairs have been considered entirely different pharmaceuticals—and other substances have shown similar, surprising differences in their left-handed and right-handed form. For example, naproxen is an anti-inflammatory drug, whose mirror-image causes liver poisoning. The drug levodopa is used to treat Parkinson's disease, but its mirror image affects the blood and can lead to chronic bacterial infections. Selegiline, another anti-Parkinson drug, has a mirror-image that is metabolized into the psychostimulant methamphetamine. And meth itself is chiral, with its mirror image being used in an over-the-counter nasal decongestant drug.

Apart from these extreme cases, most chiral drugs are simply much more potent than their mirror-image, which then constitutes an impurity. All of these examples underscore the importance of separating chiral molecules in the biochemistry and pharma industries. Improved chiral light-matter interactions are creating new ways to perform that separation.

Characterizing chiral nanomaterials

While plasmonic resonances explain chiral light-matter interactions, the descriptions above are idealized, and the optical response of actual materials will fall short of that ideal. Two specific effects are used to characterize that actual optical response in chiral nanomaterials. Both effects originate in the different interaction

In recent years, fantastic progress in nanofabrication—by both top-down and bottom-up methods—has driven rapid development of chiral nanomaterials.

between left and right CPL with the complex refractive index of the materials.

Circular dichroism. Surface plasmon resonance effects tend to be more pronounced for one direction of CPL than for the other. The difference between the two is the material's circular dichroism (CD). CD in chiral molecules and nano-objects results from the interaction of light with the imaginary part of the complex refractive index—that is, the extinction coefficient. It is related to resonant absorption or scattering.

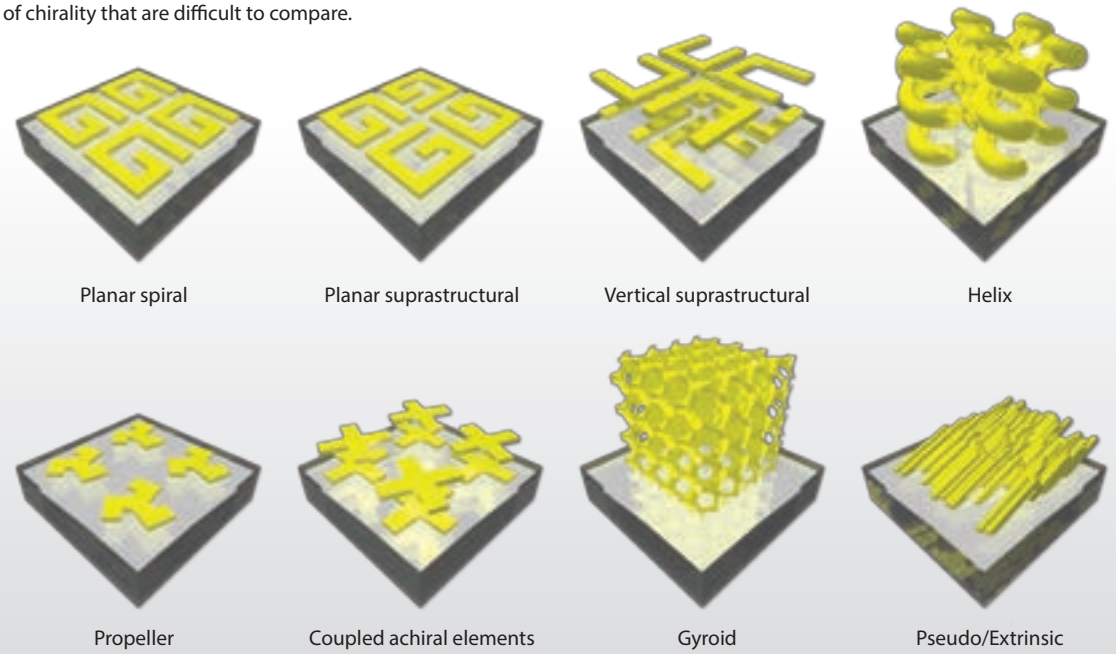
Optical rotation. Optical rotation results from the light's interaction with the real part of the complex refractive index. It occurs when, for linearly polarized light, the plane of polarization is rotated due to the presence of chirality in the nanomaterial. Measured across the spectrum, optical rotation is referred to as optical rotatory dispersion (ORD).

ORD measures the difference in phase velocity between left and right CPL. Intuitively, one would expect that CPL matching the chirality of the medium would interact more strongly with the nanostructures, causing them to re-emit light further out-of-phase with the incident light. Taking again the example of the simple harmonic oscillator, at resonance, the phase between the driving force and the oscillator experiences a pronounced transition from in-phase to out-of-phase oscillations. In the case of ORD, this can be seen as a sign change in the effect, which occurs at the center light frequency of the resonance.

From a physical point of view, these two different chiroptical effects are sensitive to different aspects of chirality. Whereas CD originates from a difference in energy transitions, ORD originates from a difference in the spatial variation of the electric field on the length scale of the molecule or nanostructure. Moreover, while nonlinear optics has counterparts to these chiroptical

Chirality at multiple levels

New nanofabrication techniques are enabling materials with different types of chirality that are difficult to compare.



effects (such as second-harmonic-generation circular dichroism [SHG-CD] and second-harmonic-generation optical rotation), these originate from the intrinsic symmetry difference between chiral pairs of molecules or nanostructures.

Thus, as linear and nonlinear chiroptical effects are sensitive to different aspects of chirality, they provide complementary information to characterize chiral nanomaterials more thoroughly. Also, nonlinear chiroptical effects are usually three orders of magnitude more sensitive than linear ones, and can be used to detect the chirality of a single molecular monolayer using tools such as SHG-CD spectroscopy. The enhancements provided by plasmonic chiral nanomaterials have made single chiral molecular monolayers measurable even with linear CD, and could in the future allow the detection of a single chiral molecule with the nonlinear effects.

A design revolution

In recent years, fantastic progress in nanofabrication—by both top-down and bottom-up methods—has driven rapid development of chiral nanomaterials. Top-down techniques include methods such as focused-ion-beam lithography, UV lithography and electron-beam lithography, in which a mask is used to print the material, as well as direct laser writing that essentially 3-D prints the nanomaterial. Top-down techniques commonly offer excellent precision and control—at the expense of time, cost and size.

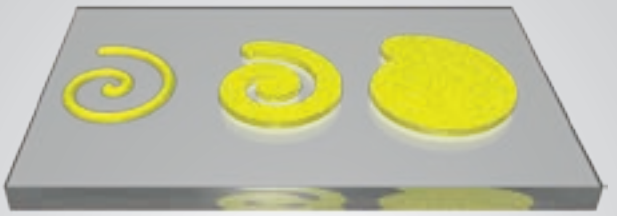
Bottom-up methods usually rely on chemical self-assembly, in which one trades control for scalability of the production. As a consequence, bottom-up methods are often considered more promising for actual technological application. Examples of bottom-up methods are colloidal self-assembly, electrochemical deposition of metals upon self-assembled chiral molecular networks and "DNA origami"—stitching together strands of DNA into scaffolds that can, for example, position gold nanoparticles into plasmonic helices with an accuracy better than 2 nm. A number of other methods combine top-down and bottom-up approaches. For instance, it is possible to guide self-assembly with laser light.

The proliferation of fabrication methods has made it possible to nanopattern metal surfaces with virtually any symmetry we can imagine. Hence it has become possible to investigate a wide range of chiral geometries. One of the most obvious chiral designs is a simple spiral, which has an inherent handedness. A chiral nanomaterial can consist of a planar array of spirals; the larger the number of spirals per unit surface, the "more chiral" this material becomes.

However, spirals can also themselves be arranged in a chiral pattern—an arrangement that endows the material with an additional level of chirality. Such "suprastructural chirality" can also evolve in the direction perpendicular to that of the planar structures. A second layer of nanostructures, for instance, might be deposited, rotated with respect to the first layer.

Other chiral designs include helices, propellers, chirally coupled achiral nanostructures and gyroids. Although all of these types of chirality have been previously seen in chiral molecules, chiral nanomaterials offer the opportunity to grow intermediate geometries—morphing one type of chirality into another, and optimizing the chiroptical response in the process.

The mere presence of chiroptical effects, however, does not necessarily imply chirality. Achiral nanostructures or molecules can give rise to chiroptical effects if the experiment itself is chiral in nature—owing, for example, to the direction of the wave-vector of light with respect to the sample surface and geometry of the material. Such material geometries are said to exhibit extrinsic chirality

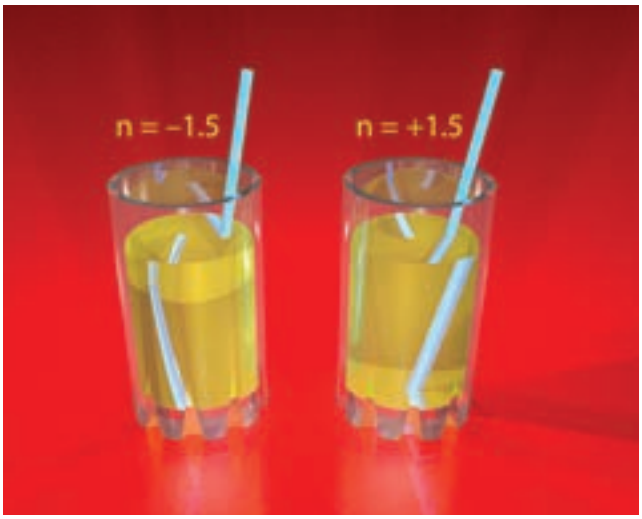


Finding chirality's sweet spot

Fructose, or fruit sugar, has a specific optical rotation of –92 degrees. Glucose (grape sugar) has a specific optical rotation of +52.7 degrees. Knowing that sucrose (table sugar) is a combination of fructose and glucose, we would expect the specific optical rotation of sucrose to be –39.3 degrees. However, it turns out to be +66.37 degrees. The difference comes from the fact that when fructose and glucose come together to form sucrose, they bond at an angle that provides an extra level of chirality.

In chemistry, it is very hard to study the emergence of chiral properties, because neither the size of the atoms nor the length and angles of bonds can be tuned. With chiral nanomaterials, however, we can prepare unit cells with a continuum of shapes between different types (or levels) of chirality, enabling the investigation of such transitions.

Nested between the length scale of the chirality in molecules and the wavelength of light, chiral nanomaterials are providing new opportunities for nanophotonic applications.



Negative refractive index

Two glasses, filled with liquids having negative (left) and positive (right) refractive indices.

(in nanostructures) or pseudo-chirality (in molecules). To characterize chirality, further chiral parameters are required; indeed, developing those parameters has been a key focus of research in chiral nanomaterials.

Increasing chiroptical effects for new applications

Chiral nanomaterials have great potential for applications in technologies that use CPL, such as quantum computation, optical communication and magnetic recording by inverse Faraday effect. In all of these, chiral nanostructures can enable the miniaturization and integration of components to manipulate the direction of CPL. Recently proposed hot-electron-injection-based ultracompact CPL detectors offer one example. More generally, CPL propagation from sources through waveguides to detectors strongly depends on the refractive index; chiral nanomaterials allow excellent control over the index. Chiral nanomaterials could enable broadband circular polarizers with an extended wavelength range at much lower cost than current alternatives. And the development of nanorobotics would greatly benefit from chiral propellers.

In the remainder of this article, we look at two developments that have attracted particular attention: the use of chirality to fashion negative-refractive-index materials; and the use of "superchiral light," a promising technology for separating chiral materials and for other sensing applications.

Negative refractive index. Achieving a negative refractive index implies gaining significant control over the permittivity and permeability of a material—which, in turn, could improve the performance of devices for manipulating electromagnetic signals. At optical frequencies, a negative refractive index could enable the fabrication of a "super lens" capable of circumventing the diffraction limit of light, and in turn enabling technological advances on the nanoscale, such as high-resolution optical nanolithography.

Chiral nanomaterials offer one promising avenue for achieving such a negative refractive index. The key to this approach is to maximize the material's so-called chirality parameter, ξ, which describes the behavior of the electric and magnetic fields in the constitutive relationships for chiral nanomaterials. In particular, the parameter appears in the expression for the refractive index of left (n^+) and right (n^-) circularly polarized light: $n^{\pm} = n \pm \xi$, where $n = \varepsilon_r \mu_r$ (the product of the material's relative permittivity and permeability). It follows that, for $|\xi| > n$, a negative refractive index can be observed for one circular polarization in chiral nanomaterials.

A structure's chirality parameter can be optimized by optimizing the interplay between electric and magnetic fields in the structure. Some of the most important adjustable factors determining the chirality parameter include the helicity of the structure, the relative orientation between elements within the unit cell, whether unit cells are connected or separated and whether individual elements within the unit cell are connected or separated. These considerations determine the Coulomb interactions, the electric resonances and the current routes, all of

which influence the chirality parameter found by solving Maxwell's equations.

Chiral materials with negative refractive index have been constructed for the microwave region, for terahertz waves and for optical frequencies. Observations from such materials can yield an experimental value for ξ, deduced from measuring the refractive index. Relating the theoretical expressions for ξ to experimental values could bring significant progress on optimizing ξ and, thus, further refining negative-refractive-index materials for practical use.

Superchiral light. Negative-refractive-index materials stem from increasing chiroptical effects by increasing the chirality of the material. But chiroptical effects can also be increased by increasing the chirality of the light itself.

For ordinary circularly polarized light, the electric field rotates at a constant rate and completes a revolution over a single wavelength. Yet we can imagine "superchiral" light in which the helical pitch of the light's electric field is compressed in some regions (nodes), at the expense of stretching it in other regions (anti-nodes). Placing a chiral molecule or nanostructure in a node of compression would be expected to enhance the chiroptical effects. In 2011, Yiqiao Tang and Adam Cohen reported on an attempt to create such an electromagnetic configuration by using a standing wave.

Tang and Cohen's work sparked considerable interest in chiral nanomaterials whose near-fields can indeed produce inhomogneous chiral densities of light. Just as plasmonic nanomaterials can compress the wavelength of light, chiral plasmonic nanomaterials can compress the helical pitch of the electric field of circularly polarized light. The superchiral light from such compression enables an enhanced chiroptical interaction with both nanomaterials and molecules.

Such enhancements lead to dramatic improvements in the performance of plasmonic chiral sensors—vital for the pharmaceutical industry. For example, in biochemical research, sophisticated molecular synthesis of even a tiny amount of chirally pure material can take months. Product is lost for the necessary testing at important stages of fabrication. Superchiral field enhancements can enhance the chiroptical signal of biomolecules, and have recently been reported to improve the sensitivity to chirality in proteins beyond conventional CD spectroscopy. That could allow faster sensing of chirality, using only the tiniest fraction of the precious product.

Moreover, using intense circularly polarized light, the enhanced chiroptical interaction offered by superchiral light makes it possible to selectively alter—or even destroy—a particular enantiomer. This would be an entirely novel approach to chiral separation. And, for some chemical reactions, the chirality of light appears to be transferable to the chemical product. This could make it possible to directly synthesize molecules with the desired chirality, depending of the choice of CPL illumination—a potentially disruptive optical technology for the chiral chemistry industry.

Nested between the length scale of the chirality in molecules and the wavelength of light, chiral nanomaterials are providing new opportunities for nanophotonic applications. Not only do they offer more efficient light-molecule interactions, but their own interplay with light leads to exciting phenomena, such as negative refractive index and superchiral light. Whereas chirality has long been considered as a Boolean left/right distinction, the detailed geometric control of chiral nanomaterials is stretching the concept—and opening up novel possibilities. OPN

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