FRONTIERS ARTICLE

Signatures of material and optical chirality: Origins and measures

David S. Bradshaw, Jamie M. Leeder, Matt M. Coles, David L. Andrews*

School of Chemistry, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, United Kingdom

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ABSTRACT

Chirality in materials and light is of abiding interest across a broad range of scientific disciplines. This article discusses present and emerging issues in relation to molecular and optical chirality, also including some important developments in chiral metamaterials. Quantifying the chirality of matter or light leads to issues concerning the most appropriate measures, such as a helicity parameter for specific chiral chromophores and technical measures of light chirality. An optical helicity and chirality density depend on a difference between the numbers of left- and right-handed photons in a beam. In connection with circularly polarised luminescence, adoption of the Stokes parameter to spontaneous emission from chiral molecules invites critical attention. Modern spectroscopic techniques are often based on the different response arising from left-handed circularly polarised light compared to right-handed light. This dissimilarity can be exploited as a foundation for the separation of chiral molecules, promising new avenues of application.

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1. Introduction

The properties of chiral molecules have interested scientists for over 150 years, ever since the discovery by Pasteur that there are two forms of tartaric acid [1]. Chiral molecules comprise non-superimposable mirror-image forms, each *enantiomer* readily identifiable by its rotation of linearly polarised light, in opposite directions for each conformer. In the natural world, many bioactive molecules are homochiral, one enantiomer predominating for reasons whose origin remains debatable, and which some claim as the basis for life [2–5]. Typically the two enantiomers behave as if physically identical, for example in NMR and IR spectroscopy, but they interact differently with other biological material or synthetic compounds of chiral form. Similar principles apply to materials that are structured on a mesoscopic scale, where a relatively new field of endeavour has arisen in the construction of metamaterials that can also exhibit chirality through larger, nano- or micro-scale architectures [6].

Since the receptors in human biology mostly consist of chiral molecules, drug action mostly involves a specified enantiomeric form. This has spurred the development, especially in the pharmaceutical industry, of a host of techniques to secure enantiopure products. Such methods, mostly multi-step and time-consuming, can typically be cast in one of two distinct categories: synthetic mechanisms designed to produce a single stereoisomer, or separation techniques to isolate distinct enantiomers from a racemic mixture. A significant drawback, for either approach, is a dependence on a supply of enantiopure reagents or substrates – synthesis routes generally utilise chiral building blocks or enantioselective catalysts [7,8], while enantiomer separation techniques typically incorporate chiral selector molecules to form chemically distinct and distinguishable diastereomeric complexes [8,9]. A key requirement in aiming to achieve enantiopure products, irrespective of the synthetic method, is therefore a means to measure, and duly quantitate the enantiomeric excess – signifying the degree of chirality within molecular products. Chiral discrimination through optical means is well-known to offer direct, non-contact ways to distinguish between molecules of different handedness, based on observations such as the subtle differences in absorption of left- and right-handed circularly polarised light, or indeed the twisting of polarisation in optical rotation. Other optical methods, under more recent development, also show some promise to achieve enantiomer separation, as will be introduced later.

In the following sections we first discuss the various measures of chirality, both for matter and for optical radiation. We then review the principles that underlie manifestations of chirality, both in conventional molecular and supramolecular materials, and in newer forms of metamaterials – some of which can, indeed, display chiral discrimination to an extent far exceeding what can be achieved with molecular substances. Following this, we then exemplify the optical characterisation of chiral matter by considering the helicity of light that such matter can produce through spontaneous

* Corresponding author.
  E-mail address: d.l.andrews@uea.ac.uk (D.L. Andrews).

emission, and we go on to discuss the new optical methods of enantiomer separation, before a final summary.

2. Measures of chirality

To begin, we briefly review a variety of methods aiming to quantify material chirality. Most such efforts, aiming to assist the design of asymmetric synthesis and chiral catalysis through the quantification of chirality, have been proposed by computational chemists and physicists, typically employing methods based on chirality functions – focusing on the mathematical properties of molecular geometry and associated symmetry point groups [10,11]. The objective of such assessments is typically to predict, and experimentally verify by optical measurement, both the value and sign of a helicity parameter that is uniquely associated with specific chiral chromophores. In optical rotation and circular dichroism, the sign of the predicted value is of particular interest as each is recognised as a pseudoscalar measure of chirality, exhibiting identical absolute value, yet opposite sign for each member of a pair of enantiomers. Methods of quantitating chirality have also been proposed using the principles of structure-activity-relationship (SAR) modelling, in which mathematical association is made between the structure of molecules and their resulting chemical or biological activity [12,13]. Nonetheless, even for any specific enantiomer, it has to be borne in mind that both optical rotation and circular dichroism exhibit dispersive behaviour, such measures of chirality varying with the wavelength of light.

As we have seen, for a system comprising just one chemical component to register its possible chirality, without involving secondary material, generally calls for optical methods. Although these offer an advantage of immediacy, the extent of chiroptical discrimination is seldom large, because the underlying mechanisms engage not only the electric field $\mathbf{E}$, but also the magnetic field $\mathbf{B}$ of the optical radiation. For later reference, we note that $\mathbf{E}$, $\mathbf{B}$ and k (the wave-vector) of light usually form a mutually orthogonal right-handed Cartesian vector set. Although both electromagnetic fields are related to a vector potential $\mathbf{A}$, through $\mathbf{E} = -\partial\mathbf{A}/\partial t$ and $\mathbf{B} = \triangledown \times \mathbf{A}$, in the UV and visible region most molecules couple strongly only with the former, electric field. It is therefore worth considering how the chirality of light itself can be quantified: building on original work by Lipkin [14], this is an issue that has attracted significant interest in the last few years [15]. The mechanisms for the engagement of optical chirality with matter will be discussed later, in Section 3.

In a quantum operator formalism, there are two terms that serve as specific technical definitions for the observable chirality of light. One is the *optical chirality density*; the other, known as the *optical helicity*, is the scalar product of operators for the vector potential and the magnetic field, $\mathbf{A} \cdot \mathbf{B}$, integrated over all space [16]. Specifically, both have been shown to depend on a difference between the numbers of left- and right-handed photons in the beam [17,18]. Indeed, Bliokh and Nori [19] have shown that the maximum and minimum values of the optical chirality correspond solely to the left- and right-handed circular polarisation light, respectively. In the case of a unidirectional, monochromatic beam, all such measures prove to be proportional to the net *spin*, ultimately associated with the spin-1 character of each photon [20]. This establishes a rigorous connection between optical angular momentum and the capacity of light to engage with material chirality. Indeed, the photon as an elementary particle (compared to massive particles) has a special capacity in this respect: its spin projection in the propagation direction is relativistically frame-invariant, and therefore it can represent an absolute basis for measures of chirality and helicity.

There are still, nonetheless, some unresolved issues connected with formulating suitable corrections for optical angular

momentum as light travels through a dielectric material medium. This problem owes its origin to the Abraham–Minkowski controversy concerning the linear momentum of light in such a medium [21–23], from which the Abraham formulation predicts a modification to the *angular* momentum of light on entry into a dielectric, while Minkowski does not. In this debate, Padgett et al. [24] supports the Abraham formulation, although they acknowledge that earlier work favours the Minkowski form, while Pfeifer et al. [25] claim that both predictions are, in practice, identical.

Despite complications in the theoretical formalism, there are numerous well-established methods that exploit the differences in response of left- and right-handed enantiomers as polarised light interacts with chiral molecules. A host of spectroscopic techniques including circular dichroism [26,27], optical rotation [28] and circular polarised luminescence [29] are based upon such disparity, as illustrated by Figure 1. Complementary techniques have also been developed based on the observation that chiral molecules can confer their optical property onto achiral material, giving rise to induced circular dichroism – the measurement of which proves particularly useful in the study of protein interaction and binding [30,31]. Nonetheless, the quantification of chirality in optical fields cannot be regarded as a direct measure of chirality in the source. Indeed there is no absolute measure of intrinsic chirality, for molecules – nor is there any conserved chiral property, in the totality of the light and matter system, in either photon absorption or emission.

It has been asserted that, for certain kinds of beam, the measure of helicity might exceed any value attributable to any conventional source of circularly polarised light – resulting in claims for the existence of *superchiral* light – but recent work has proven that this is not possible [17,18]. Superchirality has been offered as an explanation for the anomalously large signal sometimes reported in circular dichroism studies – as, for example, described by Hendry et al. [32] in their observations of proteins adsorbed onto chiral metamaterials. However, this can be explained in terms of the enhanced signal arising from the well-known surface plasmonic amplification effect in systems fabricated with a metal substrate [33,34]. Other claims that a standing wave can be generated with 'superchiral' nodes [35], by passing circular polarised light through a chiral film onto a mirror (so that the partially reflected wave interferes with the incident wave), have been shown to be consistent with a mismatch between the electric and magnetic fields of similarly superpositioned waves in the near-field region of a mirror [36].

3. Chiral metamaterials

Although the main interest of this article is molecular chirality, chiral effects have been observed in a range of other compositions such as thin film structures [37–39], with proposed applications including chiral motors [40] and memory effects in chiral domains [41]. However, it is arguably the development of metamaterials that has inspired the most recent resurgence of a broader interest in chirality. Accordingly it is appropriate to briefly consider such structures, to establish a context for some recent developments.

Metamaterials differ from naturally-occurring materials in that their composite units – which determine the optical response – are not atomic or molecular, but are usually sub-wavelength metallic structures that permit localised plasmonic resonances [42–45]. The latter engage the electromagnetic field with behaviour determined primarily by the size and shape of the fundamental units [46], and in such interactions the arrays of plasmonic sub-units behave as a homogeneous material. A common example is the split-ring resonator – a pair of sub-wavelength non-magnetic concentric split metallic rings – that is often the basis for a medium with negative refraction [47–51]. Materials with such properties, predicted by
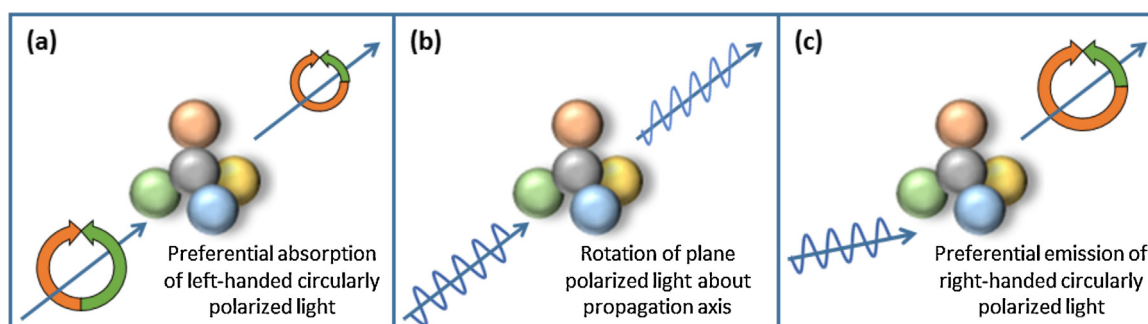
Figure 1. Interactions between polarised light and a chiral molecule. Diagrams represent the processes of: (a) circular dichroism; (b) optical rotation; (c) circular polarised luminescence (CPL). Plane polarised light is indicated by a wavy line. For CPL, either plane- or circularly polarised light can be employed in the optical excitation prior to emission.

Pendry [52] and Tretyakov et al. [53], have well-publicised potential applications including invisibility cloaking, a perfect superlens [54], and nanolevitators based on a repulsive Casimir force [55].

The description of negative index metamaterials as 'left-handed' is potentially misleading, and unrelated to its chirality meaning: in the metamaterial context it signifies that the field vectors **E**, **B** and k form a left-handed configuration [56]. Confusion may also arise on using the term 'chirality', since this could apply to multiple facets of experiments involving light and metamaterials. In essence, a structure that is 2D chiral, but which lacks 3D chirality due to its intrinsic mirror symmetry, can acquire the attributes of 3D chirality when a directionality is imposed in the third dimension, as for example by a throughput of circularly polarised light. This could arise due to the presence of a dielectric substrate in substances such as planar chiral metamaterials (PCMs) [57]. One recent study has demonstrated the chiroptical behaviour of a 'windmill'-based system comprising gold layers separated by magnesium fluoride, for example [58]. Gammadions, more widely studied, also exhibit optical activity [59] since each circular polarisation state excites different plasmonic modes in the structure, with distinctive resonances and loss factors. Similarly, achiral nanorods can be assembled on DNA scaffolding in ways to have collective plasmonic circular dichroic response [60]; examples of such structures are shown in Figure 2.

In fact, there are additional effects to be considered when beams of light with a helically structured wavefront are involved. Such beams, often known as *optical vortices*, may convey *orbital* angular momentum [61–63], as well as any spin angular momentum related to circular polarisation – in other words, an angular momentum component that is independent of polarisation states. Generally, the orbital and spin angular momentum are decoupled in the absence of matter. With sub-wavelength metallic structures, however, it is possible to tune the spin-orbit coupling of transmitted light beams [64,65]. Similarly, the construction of nanoantenna arrays according to molecular point groups allows direct generation of optical vortices; here, the sub-units must have either chiral symmetry or form PCMs [66]. Furthermore, spiral nano-structures, for example, can excite surface plasmon fields endowed with orbital angular momentum. Of course, these are evanescent waves, which decay exponentially in the direction of the surface normal; thus the angular momentum transfer is necessarily along the surface [67]. In the present connection with light endowed with orbital angular momentum, it is especially interesting that a vortex beam is shown to induce circular dichroism in non-chiral nanostructures [68].

4. Spontaneous emission from chiral molecules

The measurement of optical intensities of left- or right-handed emission is relatively routine, and chiral materials that exhibit efficient circularly polarised luminescence – a large difference in the two intensities – can provide useful probes of chirality in structures to which they bind [69,70]. Recent developments of theory, addressing differential spontaneous emission, focus upon individual chiral molecules promoted to an electronically excited state, which then decay by photon emission. It emerges that the various optical measures that might be used to quantify circularly polarised emission require particularly careful application.

One such measure assesses polarisation information in terms of a Stokes vector [71], relating to a formalism in which matrix polarimetry is commonly deployed to determine information such as the structure and relative orientation of chromophores [72,73]. The Stokes vector comprises four distinct parameters relating to wave intensities measured in different polarisation states, and for the chiral systems presently discussed, the most significant of these is S_3 – a measure of the difference in right- and left-circularly polarised field intensity. While S_3 represents a seemingly robust means to interpret chiral discrimination in the far-zone regime (where the wavelength of propagating light is much less than the distance between the source and point of detection), its adoption in the near-zone proves inconsistent with the cylindrical symmetry of the emitted radiation. Results of identical form are determined from both classical and quantum based derivations, their agreement indicating that the non-physical nature of the near-zone result casts doubt upon the short-range validity of the Stokes parameter. Alternative measures of optical helicity directly addressing the coupling between a molecular emitter and detector show features of the familiar near-zone electric dipole-dipole coupling interaction, consistent with an overall chiral dissymmetry in the coupled source-detector system.

5. Separation of enantiomers

Beyond the ability to simply quantify molecular chirality – even to detect specific enantiomers through microwave spectroscopy [74,75] – there exists a feasible means by which the interaction of an optical input with chiral chromophores can distinguish, and ultimately separate distinct enantiomers from a racemic molecular mixture [76,77]. Chiral molecular systems commonly exhibit selection rules that allow transitions to occur in which an excited state is accessible from the ground state through both electric and magnetic dipole transition moments. For example, chiral differentiation in circular dichroism relates to a cross-term that contains the pseudoscalar product of the electric and magnetic transition dipoles. Similarly, optical rotation is dependent on a tensor that also comprises a transition electric and magnetic dipole.

This type of feature can be exploited to secure, by means of a recently proposed mechanism, the optical separation of enantiomers – the basis for which is shown in Figure 3. In particular, the forward – Rayleigh scattering process engages circularly polarised
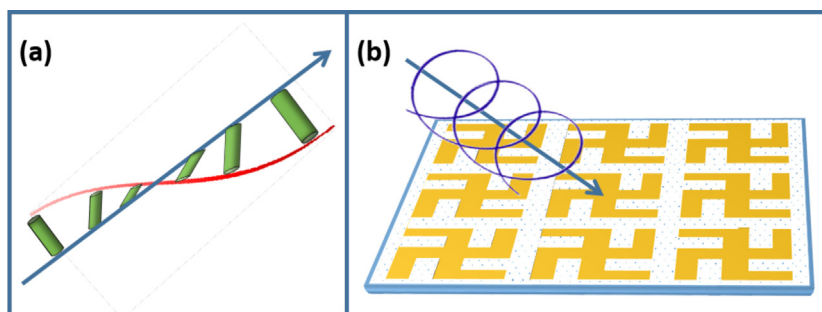
Figure 2. Circularly polarised light impinging on: (a) staggered nanorods: the absorption is strongest when the period of rotation of the nanorods matches the optical wavelength; (b) an array of metallic gammadions on a surface, manifesting chiral differentiation against light of the opposite handedness.
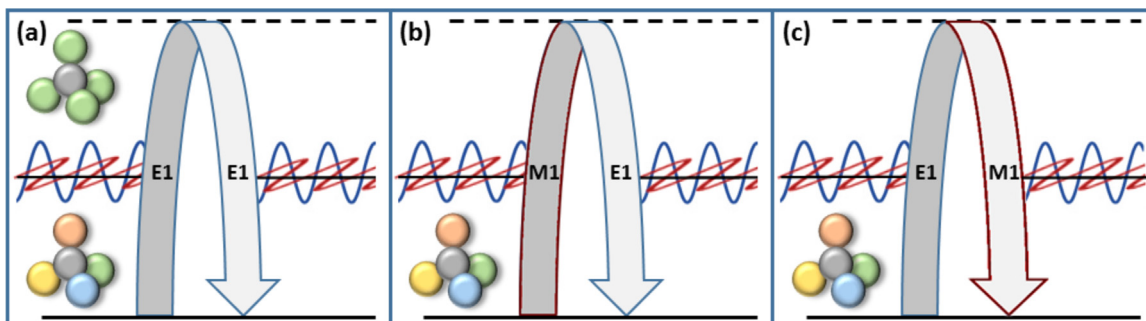

Figure 3. Energy level diagram depicting forward Rayleigh scattering of light with an arbitrary polarisation, its electric and magnetic fields indicated by blue and red waves, respectively. One photon is annihilated and an identical photon is created, through interactions that entail: (a) electric dipole transition moments for absorption and emission events – the most physically important mechanism but a non-contributor to chiral discrimination; (b) a magnetic dipole for absorption and electric dipole for emission; (c) vice versa. The latter two cases, which arise only for non-centrosymmetric molecules, despite being lower-order and implying a much weaker interaction than (a), are the leading non-zero contributions in chiral discrimination studies.

light, introducing physics that is connected to the optical trapping of chiral molecules. Semiclassically, this might be described as a manifestation of a dynamic (ac) Stark effect: the optical trap produces an energy lowering of the molecule due to the presence of the irradiating electromagnetic beam. In detail, it has been shown that circularly polarised light of a specified helicity will produce a different potential energy, and hence a different optical force, when interacting with a left-handed compared to a right-handed enantiomer. This chiral discrimination provides a physical basis for the optical separation of enantiomers, in which one enantiomer is driven more than the other towards a local intensity maximum (or minimum) of the irradiating beam and, thus, produces a difference in the time-averaged concentrations of the two enantiomers. Such a differential force is small (with estimates in the 10^{-16} N range for an input laser beam intensity of 5×10^{11} W cm^{-2}) but experimentally attainable. A potential physical system is given by Figure 4.

Several other groups have tackled alternative methods of harnessing chiral forces to achieve enantiomer separation. For example, at the micron scale, an optofluidic experiment to separate chiral materials has been reported by Tkachenko and Brasselet [78], although related nanoscale studies have yet to be realised. Theory on molecular-level chiral separation is increasingly expansive, and includes notable descriptions by Jia and Wei [79], Canaguier-Durand et al. [80,81] and Cameron et al. [82,83].

6. Discussion

The extent of interplay between the fields of material and optical chirality is now expanding, and at an accelerating pace, well beyond the most familiarly associated spheres such as optical rotation. Part of the drive for many of the recent advances can be attributed to developments in metamaterials; advances in theory and in optical technology are also both contributors to the progress. Taking an overview of high level theoretical and technical advances, it is clear that that much of the current work promises foundations for entirely new realms of application, based on the fundamental property of chirality.
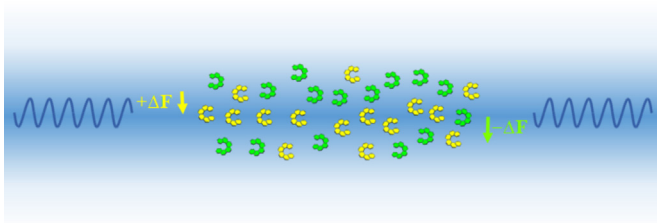
Figure 4. Diagram depicting the relative positions, within a circularly polarised trapping beam of Gaussian profile, of two typical enantiomers (L)-hexahelicene (yellow) and (R)-hexahelicene (green). Left-handed molecules have a greater tendency, compared to the right-handed ones, to be positioned towards the centre of the Gaussian beam, as denoted by the chiral force Δ**F**; blue wavy line denotes the throughput beam.

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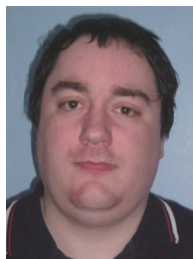
David S. Bradshaw is a postdoctoral researcher who received his PhD from the University of East Anglia in 2006. He has co-written over 60 papers, including book chapters and a magazine article. His research currently focuses on resonance energy transfer and optomechanical forces. He is a Member of the Institute of Physics and the Royal Society of Chemistry.

Jamie M. Leeder works as a postdoctoral researcher in the Nanophotonics and Quantum Electrodynamics group based at the University of East Anglia. He is currently developing novel theory relating to the design of photonic mechanisms and optical characteristics in nanostructured materials. Jamie enjoys productive affiliations with the Institute of Physics and the International Optics and Photonics Society (SPIE).

Matt M. Coles completed his PhD in January 2014 after studying at the University of East Anglia (UEA). He then held research positions at the Max Planck Institute for the Physics of Complex Systems and Imperial College London, and is now an Honorary Research Associate at UEA. His research interests are currently optical vortices, chirality and nonlinear optics.

David L. Andrews is Professor of Chemical Physics at the University of East Anglia, where his group conducts research on fundamental photonics, optomechanical forces, optical vortices, nonlinear optics, energy harvesting and molecular energy transport. He has more than a dozen books and over 300 research papers to his name. David Andrews is a Fellow of the Institute of Physics, the Royal Society of Chemistry, and SPIE – the international optics and photonics society.