

# Circular Polarization of Luminescence as a Tool To Study Molecular Dynamical Processes

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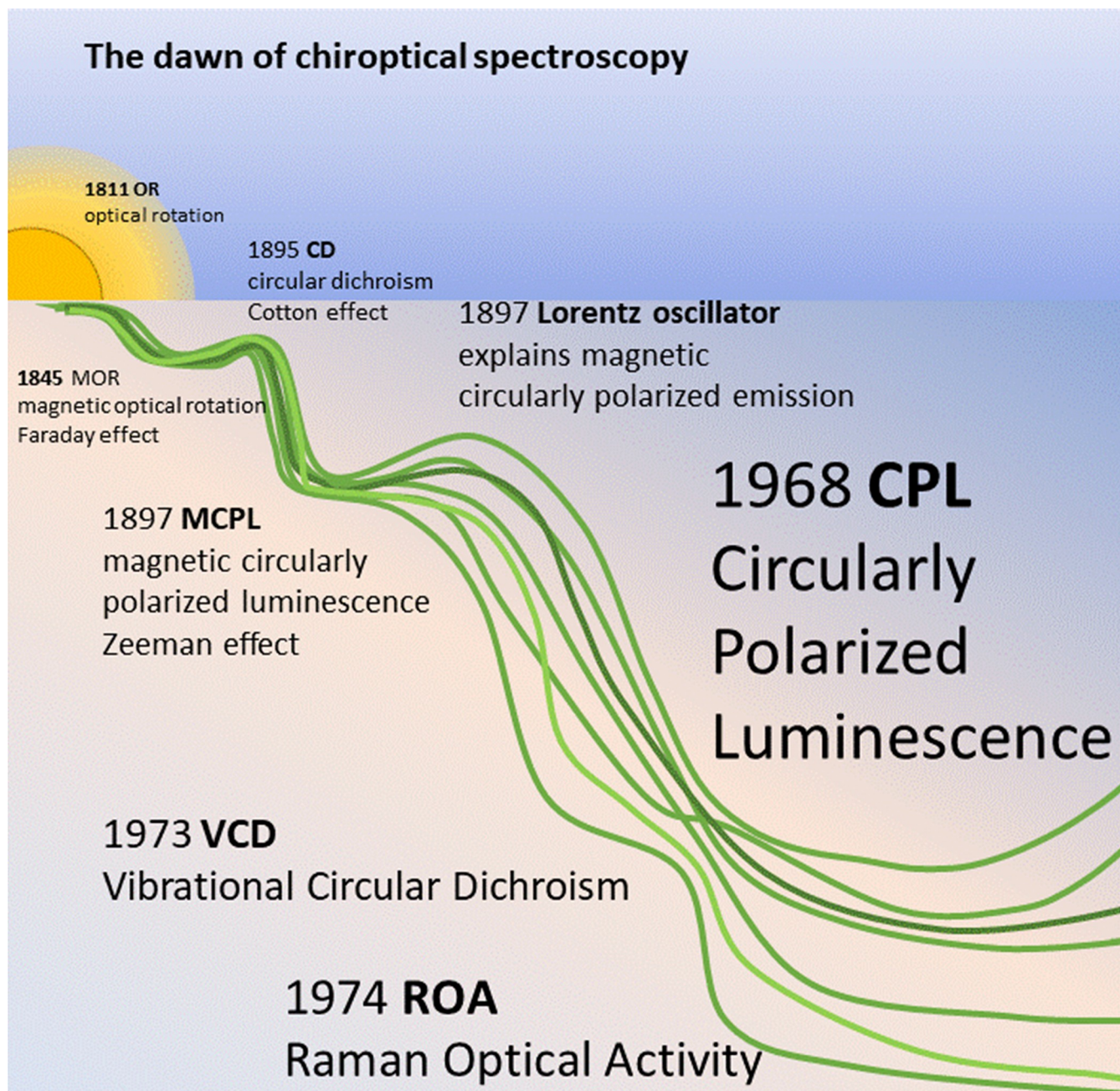
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# Circular Polarization of Luminescence as a Tool To Study Molecular Dynamical Processes

Stefan C. J. Meskers<sup>\*[a]</sup>*Dedicated to Harry P. J. M. Dekkers on the occasion of his 80th birthday*

Circular polarization of luminescence is a phenomenon that can be observed for chiral molecules in isotropic solution, for molecular aggregates and molecular materials. Also, the electroluminescence from chiral molecular materials in organic light emitting diodes can be nearly completely circularly polarized. In this review we focus on the latest developments in experimental results for the categories listed above. A unifying description of the origin of the circular polarization is still missing. We

revisit the very earliest efforts to measure and understand circular polarization in light emission in order to better understand the present day confusion on the origins of the polarization. It seems that quantum field theory of electromagnetic interactions could provide leads for a comprehensive description of the circular polarization including contributions from helicity at all possible length scales from the molecular to the macroscopic.

## 1. Introduction

In 1967, Cees Emeis and Luitzen Oosterhoff reported for the first time measurement of the circular polarization of luminescence (CPL) from chiral, enantiomerically resolved molecules in solution.<sup>[1]</sup> Chiral molecules, i.e. molecules whose mirror image structure cannot be brought to overlap with the original, emit left and right circularly polarized light with different probabilities when in an isotropic solution. Since this first pioneering report, the research field on CPL has steadily grown.<sup>[2-5]</sup> Especially after the turn of the millennium, when CPL spectrometers also became commercially available, a rapid spur in number of reports of circularly polarized emission has occurred. To date, a large number of molecules, molecular aggregates, supramolecular systems and materials have been investigated. The experimental data gathered have deepened our understanding of the molecular aspects of the CPL phenomenon. Yet on the supramolecular level our grasp of the circular differential emission is less firm and confusion looms.


For small molecules, the *degree* of circular polarization, i.e. the relative difference in the intensity of the left and right circularly polarized luminescence can be quite large for weakly allowed transitions. For strongly allowed transitions of dispersed molecules with low molecular weight, the degree of circular polarization is almost invariably quite small, on the order of  $10^{-3}$  or less. This indicates that the circular polarization is associated with the breakdown of the electric dipole approximation. The semiclassical picture of the emitting molecule as a linear Lorentz oscillator is no longer accurate for the weakly allowed transition and the variation in strength and direction of electromagnetic fields over the volume occupied by the molecule has to be included, according to an argument that can be traced back as far as Boltzmann.<sup>[6]</sup> The description of the spectroscopic transition needs to be extended to also include a circular or rotational component in the movement of


the oscillating charge on the molecule. The combination of circular motion together with linear translation of charge then provides an intuitive picture of a charge undergoing oscillatory motion along a helical path in the chiral molecule. The circularly polarized luminescence from isolated molecules is understood in terms of a combination of electric and magnetic transition dipoles representing resp. the linear and circular aspect of the motion of the oscillating charge in the spectroscopic transition.<sup>[2]</sup>

The combination of an electric with a magnetic transition dipole pointing in the same direction leads to the emission of light with a left-handed circular component. A magnetic transition dipole antiparallel to the electric dipole leads to a right-handed circular polarization. To see why this happens one only needs to consider that the oscillating magnetic dipole will generate an electromagnetic wave with magnetic field parallel to the dipole. Associated with this magnetic wave will be an oscillating electric wave with polarization perpendicular to the magnetic dipole and the direction of propagation. The electric component of the oscillating electric dipole combined with the electric component from the oscillating magnetic dipole yield the x and y components of the electric field of a circularly polarized electromagnetic wave travelling in the z direction electric dipole. The oscillation of the magnetic dipole moment naturally has a phase lag of  $90^\circ$  with respect to the electric dipole oscillations. This follows from the harmonic oscillatory motion of the electron along a helical path where position along the helical axis and velocity are  $90^\circ$  out of phase. Alternatively, we know from quantum mechanics that the electric dipole operator is fully real while the magnetic transition dipole operator incorporates the angular momentum which contains the imaginary number  $i$ . Thus, on the complex plane the phase factor  $i = e^{i\pi/2}$  of the magnetic transition dipole relative to the electric dipole corresponds to a phase difference of  $90^\circ$ . This phase lag of the magnetic dipole translates into the characteristic phase difference between x and y components of the electric field of circularly polarized light.

Achiral dye molecules embedded in a chiral environment provided by a cholesteric liquid crystal can show very large and sometimes even nearly complete circular polarization of their fluorescence even when the molecular transition is fully allowed.<sup>[7]</sup> For these materials, an explanation of the circular polarization in terms of molecular electric and magnetic transition dipole moments is not feasible. Here the circular polarization must arise from a wider sphere of influence including the surrounding medium for the luminophore. An

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 An invited contribution to a Special Collection on Circularly Polarized Luminescence

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explanation of the circular polarization in terms of the optical properties of the molecular environment rather than the transition dipole moments of the emitting chromophore seems more appropriate for these cholesteric materials.

After considering the above two extreme cases, one may recognize that in the supramolecular assemblies and molecular aggregates that have become amenable to detailed spectroscopic study thanks to progress in the field of supramolecular chemistry,<sup>[8,9]</sup> the distinction between the photon-emitting molecular center and off-resonant surrounding is often impossible to make. Thus, the mesoscopic structures may constitute an intermediate case where the circular polarization could originate partially at the site of photon emission and partly from passage of the emission light out of the structure with long range helical order. It is for these intermediate cases that confusion can easily arise with regards to the proper interpretation of the polarization of the luminescence.

In this review, we will first attempt a *deconstruction* of our understanding of the CPL phenomenon by peeling back the layers of interpretation that have been drawn over the basic experimental observation.<sup>[10]</sup> It turns out that the historical context of the first CPL measurement by Emeis and Oosterhoff provides a convenient path to arrive at a less differentiated, more primitive yet also broader understanding of the polarized emission. Next, we will look at the technical developments in the measurement of CPL, followed by a review of recent experimental results. Finally, in a discussion section we will combine the fruits of the deconstruction to the experiments on mesoscopic structures to an attempt to identify possibilities for fresh development outside the current paradigmatic viewpoints centering around individual molecules or macroscopic optics.

## 2. Some Basic Theoretical Considerations

What prompted Emeis, then a graduate student, and Oosterhoff, his supervisor, to look for circular polarization in the luminescence of molecules? A clue is provided by preceding scientific investigations and investigators at Leiden university where the first CPL measurements were carried out. Oosterhoff had done his own Ph.D. also in Leiden working with H.A. Kramers. Kramers in turn had been an undergraduate student



The author became familiar with circular polarization of luminescence during his Ph.D. research on chiral lanthanide complexes and biomolecules at Leiden university. When still a student at the same university, he learned how to gauge the electromagnetic potential and switch between reference frames when following a course on quantum field theory at the Lorentz institute. These two events have been a continuous source of inspiration for research on optoelectronic properties of molecular materials. Currently, the author is affiliated with Eindhoven University of Technology as associate professor.

of H.A. Lorentz in Leiden, had done his thesis research with Niels Bohr in Copenhagen and defended his thesis on the polarization properties of transitions in the hydrogen atom in Leiden with Paul Ehrenfest as promotor. Eventually Kramers would succeed Ehrenfest as the chair on theoretical physics who in turn had replaced Lorentz.

Lorentz is well known for his explanation of the splitting of the spectral D-line of sodium by a magnetic field as observed by Zeeman. The split lines of the Na atom correspond to emission with left and right circular polarization. In a broader perspective, Lorentz developed electron theory i.e. the interpretation of Maxwells electromagnetism in terms of an elementary charged particle. This effort contributed to the development of quantum field theory but also to atomic and molecular spectroscopy. Emission and absorption of light could now be attributed to oscillation of harmonically bonded charge in materials, i.e. in terms of Lorentz oscillators. In a sense, the CPL from molecules provides experimental evidence for an extended Lorentz oscillator model with the electron moving along a helical path. So, all the elements necessary for development of CPL seem to have been present in Leiden very early on in the first decades of the 20<sup>th</sup> century. So why did it take so long for the first CPL measurements on molecules to emerge? And perhaps more importantly, why is our understanding of the circular polarization in larger aggregates still so murky? The answer is that extension of Lorentz oscillator model to an electron moving along a helical path is far from trivial: enter Albert Einstein.

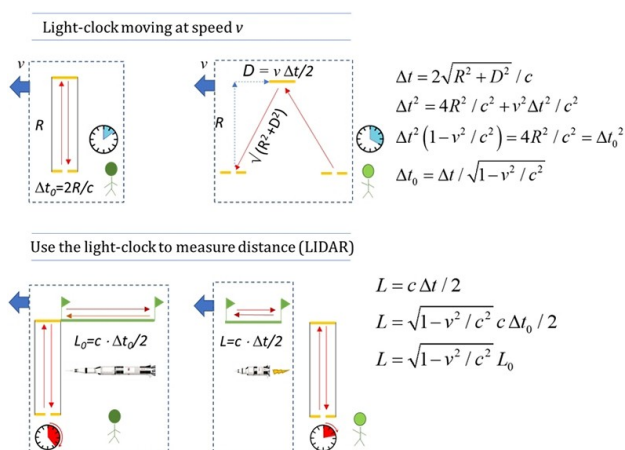
Lorentz and Ehrenfest were good friends with Einstein and the latter spent some semesters in the 1920's as guest professor in Leiden. His views of relativity were taken up in ongoing research in Leiden on electro-magnetism, field theory and cosmology. The work on relativity has had far less influence on molecular science and spectroscopy. Yet, as I will try to demonstrate below, we can still obtain useful insights from applying special relativity to molecular luminescence. So let's try to restore the broken connection. As we will see this will lead to *paradoxes*, three of which will be formulated below. At the end of this review, we will come back to these paradoxes and see whether they can be resolved.

How would Einstein or Lorentz have thought about the circular selective emission or absorption of light by chiral molecules? According to legend,<sup>[11]</sup> Einstein got inspiration for his special relativity by imagining how the universe would look like to an observer travelling together with a photon at the speed of light. In analogy, we can now ask ourselves: How would a chiral molecule look like to as seen by an observed travelling at the same speed as a photon in vacuum?

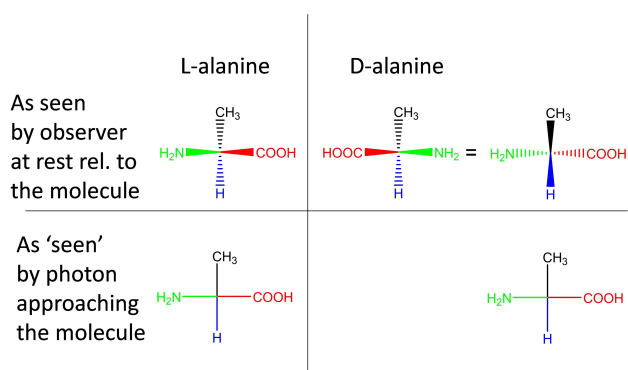
### 2.1. Paradox I

How would a chiral molecule look like as seen by an observed travelling at the same speed as a photon in vacuum? Such an observer would see the chiral molecule approaching at the speed of light and according to the special theory of relativity, the molecule would appear contracted in length, due to the so-

called Lorentz contraction. See Figure 1. From the vantage point of the photon, the Lorentz contraction would be complete, and the chiral molecule should appear as a flat pancake. This contraction will eliminate the 3D chirality of the molecule and the two mirror-image related forms of the chiral molecule will be indistinguishable when viewed under the same orientation. See Figure 2. So, paradoxically, how could a circularly polarized photon ever distinguish between the left and the right handed form of a chiral molecule?



**Figure 1.** The Lorentz contraction. Using a rod of length  $R$ , we can build an elementary light-clock, by watching how long it takes for a light flash to be reflected back by a mirror at the end of the rod. An observer moving together with the clock sees the light flash return after a time interval  $\Delta t_0$ . Another observer who sees the clock moving at speed  $v$  will see the flash reappear after  $\Delta t$ , a time interval shorter than  $\Delta t_0$ . Thus, a moving clock appears to tick more slowly than a stationary one. The light-clock may now be used to measure the length  $L$  of, say, a rocket. An observer in the moving rocket will measure  $L_0$  with his own moving clock on board of the spaceship. An earth-based observer who sees the rocket moving away at speed  $v$  will measure length  $L$  with his own earth-bound clock. Because the latter, stationary clock ticks faster than the moving clock in the rocket, the observer on earth will find a length  $L$  of the rocket is shorter than  $L_0$  by a factor  $\sqrt{1 - v^2/c^2}$ . This is known as the Lorentz-Fitzgerald contraction.<sup>[12]</sup>



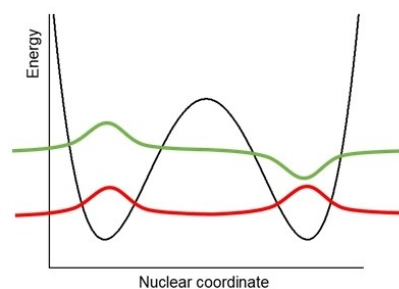
**Figure 2.** The chiral molecule alanine occurs in two different enantiomeric forms L and D that can be distinguished by an observer at rest relative to the biomolecule. In an Einsteinian thought experiment however where we look at the molecules as seen by an observer travelling toward the molecule along a direction perpendicular to the paper at the same speed as a photon in vacuum  $c$ , the molecule would appear to be completely flat because of the Lorentz contraction so that the D an L form can no longer be distinguished.

## 2.2. Paradox II

Suppose that we send a right circularly polarized photon through a medium, e.g. a solvent. Because of the refractive index  $n$  of the solvent being larger than unity, the effective speed (phase velocity) of the photon is now reduced relative to that of vacuum to a value  $c/n$ . Now to an observer moving at a velocity  $v$  close to the speed of light  $c/n < v < c$ , the lightwave in the solution will appear to propagate backwards and will therefore appear to have a circular polarization opposite to the polarization as perceived by observer at rest in the laboratory frame of reference. The two observers will not agree over the handedness of the lightwave. Apparently, the circular polarization of the light wave travelling at reduced speed is not ideal and so it cannot be completely circularly polarized. If the light emitted or absorbed by the chiral molecule in solution is never truly circularly polarized how can we then understand CPL?

## 2.3. Paradox III

One of the primary goals of molecular spectroscopy is to explain spectroscopic transitions of a molecule in terms of its structure. Within the research field one presupposes the existence of molecular structure. Yet is this presumption justified; do chiral molecules really have a structure? As Friedrich Hund already pointed out in 1927:<sup>[13,14]</sup> a chiral molecular structure cannot be the true eigenstate of the Hamiltonian of the molecule since the Hamiltonian is invariant under spatial reflection. Therefore, also the eigenstates must have a defined parity under spatial reflection. The enantiomeric, mirror-image related forms do not possess this required symmetry property. The true eigenstates of a chiral molecules in perfect isolation should therefore be quantum mechanical superpositions of the left and right-handed form of the molecule. The potential energy landscape for a chiral molecule, in some respects resembles a double minimum potential energy well with left- and right-handed forms being minima of equal energy. For a double well potential, the lowest true eigenstates feature an in-phase combination and out-of-phase combination of probability densities centered around the two minima. See Figure 3. The question thus arises how and when do certain chiral molecules appear as one particular separate stable enantiomeric form?<sup>[15]</sup> This question is closely associated with



**Figure 3.** Lowest energy eigenstates in a double minimum potential well.

the collapse of the wavefunction of a quantum system upon a measurement in the Copenhagen interpretation of quantum mechanics.<sup>[16,17]</sup> As is well known Einstein had reservations against this interpretation.

The question of molecular structure can be formulated even broader than the example of the two enantiomeric forms discussed above. For any molecule that has two or more low energy isomeric forms, the question arises whether a single nuclear geometry is an accurate representation of the actual physical entity. For circular polarization of luminescence, the problem of molecular structure is even more acute, because the energy of the emitting state is uncertain. Especially in condensed media, part of the excitation energy provided to the molecule is dissipated quite rapidly via interactions with the surrounding molecules. Therefore: is it really possible to interpret the circular polarization of luminescence in terms of (a) molecular structure?

## Experimental Methods

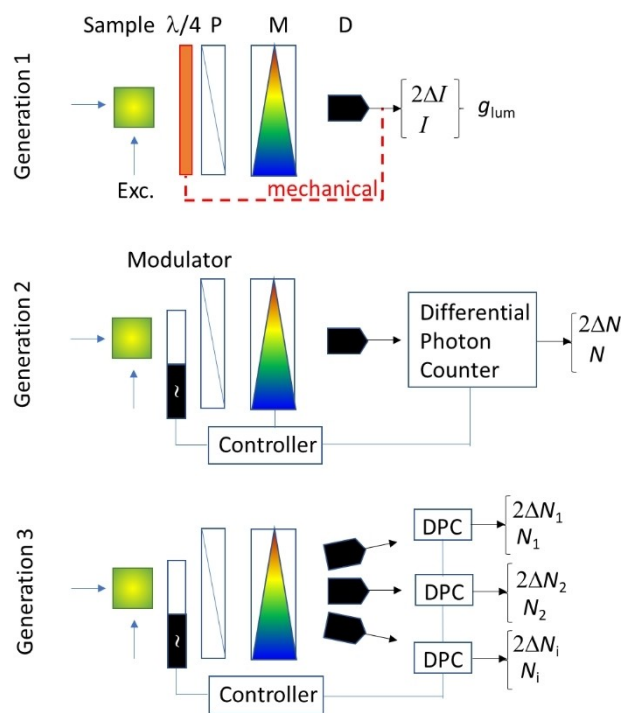
Quantitative measurements of the intensity luminescence from molecules, molecular assemblies and molecular materials are notoriously difficult. Relative emission intensities are much easier to determine. Because of this difficulty, the experimental characterization of CPL focusses on the determination of the relative difference in the intensity of left and right circularly polarized luminescence. The results are usually expressed as dissymmetry factor,  $g_{lum}$  [Eq. (1)]:

$$g_{lum} = \frac{2(I_L - I_R)}{I_L + I_R} \quad (1)$$

Here  $I_{L(R)}$  stands for the intensity for left(right) circularly polarized luminescence usually recorded in a particular wavelength interval and specific range of emission directions of the emitted photons. To determine  $g_{lum}$  experimentally, various experimental layout have been used, see Figure 4.

In the first generation of instruments, a circular analyzer made by the combination of a quarter waveplate and a linear polarizer, is employed to distinguish the left from the right circularly polarized. The circular analyzer is switched mechanically by rotating the quarter waveplate over 90°. The major drawback of this layout is the sensitivity to low frequency fluctuations in e.g. the intensity of the excitation source noise. Nevertheless this scheme works well for highly circularly polarized emission and can easily be integrated with time-resolved detection.<sup>[18,19]</sup>

In the second generation of instruments, a high frequency polarization *modulator* is used to discriminate between the two polarizations.<sup>[20]</sup> The photoelastic modulator invented by Kemp<sup>[21]</sup> in combination with a polarizer can be used as an analyzer that switches between left and right circularly polarized at high frequency (usually 50 kHz). The modulator can be operated at moderate applied voltages but has a fixed frequency set by the mechanical resonance of its active amorphous quartz optical element. Because of the high-frequency polarization modulation, the electrical signal coming from the emission detector now needs to be processed electronically in order to extract the circular differential intensity.<sup>[22]</sup> This can be done in an analog fashion using a lock-in amplifier.<sup>[23–26]</sup> Yet for low intensity luminescence signals this can be troublesome. To solve this issue with low intensities,

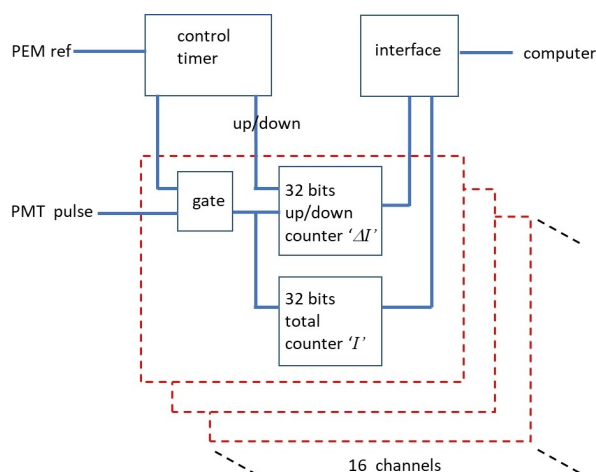


**Figure 4.** Three generations of experimental setups for recording the circular polarization of luminescence for molecular compounds.  $\lambda/4$ : quarter wave plate, P: polarizer, M: monochromator, DPC: differential photon counter.

Dekkers and Schipper introduced digital processing of the recorded luminescence signal intensity.<sup>[27]</sup> Using a photomultiplier tube and an appropriate discriminator one can count individual pulses in photocurrent induced by a single incident photons. The reference signal provided by the modulator allows one to reconstruct the polarization phase of the modulator. By using appropriate electronic gates, one can then accept only pulses from photons emitted when the modulator had sufficient circular modulation depth. The selected pulses can then be sorted according to their circular polarization (L/R) and counted separately. This digital photon counting detection scheme gives a stable baseline at the  $|g| = 10^{-5}$  level and provides direct access to the  $g_{lum}$  value. As an additional bonus when using such a differential photon counter (DPC), the standard error for  $g_{lum}$  can usually be predicted accurately from the total number of photons counted ( $N$ ) following Poisson statistics  $\sigma(g_{lum}) = 2/\sqrt{N}$ .

In the latest generation of instruments, multiple wavelengths are monitored at the same time. This considerably reduces the measurement time required for a full spectrum. This detection scheme requires an array detector. Various types of such array detectors are available. Yet many of these arrays use a serial readout process which makes the total readout time of the full array quite long. For instance, the relatively slow readout of a conventional CCD detector makes it difficult to combine this type of detector with high frequency polarization modulation of the PEM (50 kHz). Photomultiplier array detectors can be read out in parallel and are compatible with high frequency modulation with the PEM. In the latest type instrument developed by Dekkers and coworkers, 16 channels are monitored in parallel, see Figure 5.

As an alternative to the PEM, modulators that can be operated at lower frequency have been combined successfully with a CCD based detection. This allows for a large number of channels, allowing for mapping of the entire spectrum with high resolution.



**Figure 5.** Schematic layout of the parallel signal processing in the multi-channel CPL spectrometer. PEM photoelastic modulator, PMT photomultiplier tube.

This detection scheme has been optimized for detection of Raman optical activity where a high-resolution coverage of the entire spectrum is desired to resolve all the Raman bands. Here an electro-optic modulator based on the Pockels effect can be used.<sup>[28]</sup> Also liquid crystal modulators may be employed. The liquid crystal modulators can be operated at much lower driving voltages ( $\sim V$ ) than the Pockels type element ( $\sim kV$ ).<sup>[29]</sup> Circular polarization of luminescence has been successfully recorded using a Raman optical activity instrument.<sup>[30]</sup>

As an alternative to modulation methods where left and right polarized photons are separated in the time dimension, the two circular polarizations may also be separated in a spatial dimension. Such spatial separation is possible with e.g. a Wollaston prism or a Rochon prism and has recently been applied.<sup>[31]</sup> The spatial separation of the circular polarizations makes the most efficient use of emitted photons and eliminates the time restrictions on the readout of the detector. Spatial separation is thus fully compatible with e.g. a CCD camera. A disadvantage of the spatial separation may be that it requires quite careful calibration of the baseline because the two separate sets of detectors for left and right may have slightly different efficiencies for detection of a photon.

Starting in the 1990s, experimental methods to measure CPL as function of time after pulsed excitation have been developed. This development is driven mainly by the discovery that CPL can be used to study racemic mixtures through preferential excitation of one enantiomer by illuminating with pure circularly polarized light.<sup>[32,33]</sup> By addition of time resolution, the racemization kinetic in the excited state can be measured directly without the need of chemically resolving the luminophore into its two mirror-image related forms. This allows for the study of chiral compounds that racemize very rapidly on a ms timescale rapid, as has been accomplished for the labile *tris* complex of europium with 2,6-pyridinedicarboxylate.<sup>[34]</sup>

Time resolution methods such as time-resolved single photon counting, can be introduced into the CPL instrumentation of generation one with comparative ease. Here one measures the complete luminescence decay trace for one circular polarization and then switches the analyzer and records the other decay trace. For compound with very high  $g_{lum}$  values such as e.g. lanthanide chelates, this has been implemented successfully.<sup>[16,17]</sup>

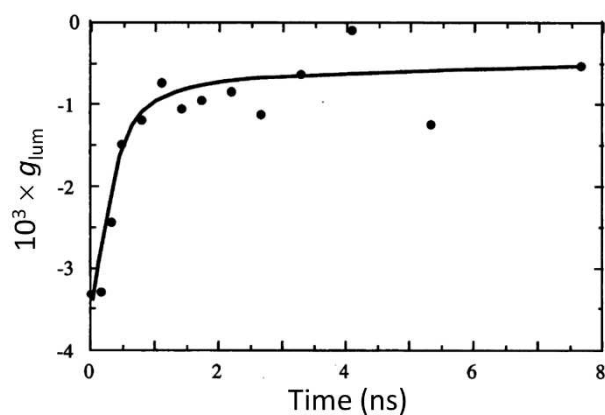
However, for signals with lower  $g_{lum}$ , high frequency polarization modulation is preferable for better baseline stability. In instruments of the generation 2 incorporating polarization modulation with a PEM and differential photon counting, time resolution can be introduced via an additional electronic gate to select only photons in a particular time window after pulsed excitation.<sup>[35]</sup> The signal collection efficiency may be improved greatly by collecting all photopulses using multiple time channels.<sup>[36–39]</sup> The time-resolved instruments developed in Charlottesville, Leiden and Ann Arbor, rely on fully random placement of the excitation light pulses in the modulation cycle. In this way a time resolution better than the modulation period of the PEM (20  $\mu s$ ) can be realized. Currently, the highest time resolution reported is that of nanoseconds,<sup>[40]</sup> see Figure 6. Nanosecond time resolution opens up the possibility to study dynamic processes in the lowest singlet excited state of organic dye molecules.

## Applications

### Scope of the CPL technique

Circular polarization of luminescence measurements can be applied to molecules, molecular aggregates or materials that emit light upon electronic excitation by any means. For instance, circular polarization measurements are regularly applied to photoluminescence via spin-allowed radiative transitions but also delayed fluorescence, phosphorescence,<sup>[41,42]</sup> chemiluminescence<sup>[43,44]</sup> and bioluminescence<sup>[45]</sup> can be studied. Most recent is the detection of circular polarization in electroluminescence<sup>[46]</sup> and cathodoluminescence.<sup>[47,48]</sup> CPL measurements also apply to molecular species that do not exist in the electronic ground state, such as excimers<sup>[49–53]</sup> and exciplexes.

Chiral molecules emit circularly polarized luminescence. Yet the reverse of this statement is not necessarily true. Emission of circularly polarized light is not exclusively limited to chiral objects. Also achiral molecules may emit circularly polarized luminescence. Some of the most exciting new developments in the field involve nominally achiral materials involving spin polarized electrons and holes, e.g. spintronics.



**Figure 6.** Time-resolved circularly polarized fluorescence of NADH bound to LADH in a binary complex. Reproduced with permission from ref. [40]. Copyright 1995. National Academy of Science.



Obviously with CPL one probes the subset of electronically excited states. By careful choice of excitation conditions, this population of excited species may have a lower symmetry than the totality of chromophoric sites. For instance, using circularly polarized excitation light, one enantiomer in a racemic mixture may be excited preferentially resulting in circularly polarized emission.<sup>[28,54]</sup>

Also achiral molecules may emit circularly polarized luminescence. Various mechanism may contribute to this remarkable effect. The first mechanism closely related to the circular polarization from racemic mixtures mentioned above. Some achiral molecules actually contain two mirror image related chromophoric parts. If these two parts are sufficiently weakly coupled electronically, they will behave as separate racemic chromophores. By selectively exciting the chromophoric part of one particular handedness, one can record circularly polarized luminescence. Such selective excitation may be achieved using circularly polarized excitation light<sup>[55]</sup> or by using a chiral chemiluminescent precursor molecule.<sup>[42]</sup>

A second mechanism for CPL from achiral systems is well known from semiconductor physics and involves spin polarized charge carriers in quasi-2D structures induced by circularly polarized optical excitation. The first systems in which these effects became apparent were quantum wells within bulk material.<sup>[56]</sup> More recently also 2D transition metal chalcogenide monolayers have been shown to emit circularly polarized light upon circularly polarized excitation.<sup>[57–61]</sup> Here it should be noted that the circular polarization of the emission cancels when averaging over all emission directions. The excitons generated by the circularly polarized excitation, have a net angular momentum and emit left- and right-handed circularly polarized photons in the different directions pointing upward and downward from the 2D layer.

A third mechanism for CPL from achiral molecules or materials is even more general and does not involve any selective excitation of parts of the material. For crystals it has long been known that optical activity (including optical rotation, circular dichroism and CPL) is possible for some non-enantiomorphous crystals.<sup>[62–64]</sup> The first reports with experimental support for this notion are noteworthy.<sup>[65–67]</sup> Using abstract tensor analysis it is predicted that four non-enantiomorphous crystal classes allow for optical activity see Table 1.<sup>[68]</sup> Although tensor analysis is a very powerful method, it may not be particularly insightful to people accustomed to think in terms of molecular structure. Therefore, we will now sketch a more

Crystal class	Point group	Example
m	$C_s$	acrolein
mm2	$C_{2v}$	cis-butadiene (planar)
$\bar{4}$	$S_4$	1,3,5,7-tetrachlorocyclooctatetraene
$\bar{4}2m$	$D_{2d}$	cyclooctatetraene

intuitive picture of how circular polarization can arise in spite of mirror image symmetry elements or inversion being present.

The four classes allowing for optical activity despite being achiral are each based on different a point group, see Table 1. In Table 1 we also list examples of molecules with structure belonging to these points group. As first example we look at cyclooctatetraene, see Figure 7.

By looking at the cyclooctatetraene from the two particular angles shown in Figure 7, it is immediately obvious that structure harbors opposite helicities along different directions. Now for a photon emitted in a direction parallel to one of the axes with a specific helicity, the polarization will have an imprint of the helicity along that direction. This means that the cyclooctatetraene can emit circularly polarized photons, but when averaging over all possible directions the circular polarization will exactly cancel out.

We can now spell out the argument for circularly polarized emission from achiral molecules in more physical detail. For this we look at cyclobutadiene in its fully planar conformation belonging to the  $C_{2v}$  point group, see Figure 8. Also here one may recognize opposite helicities when looking at the molecule from different angles. We can then look at the optical transition

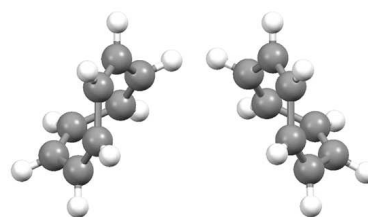


Figure 7. Cyclooctatetraene, an achiral molecule with  $D_{2d}$  symmetry.

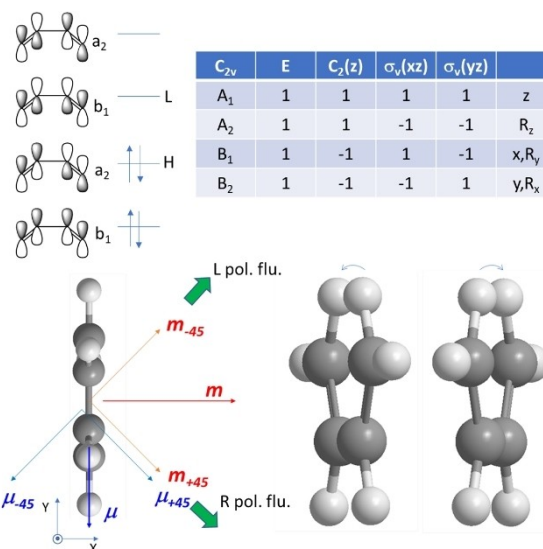


Figure 8. Cyclobutadiene in a fully planar, cisoid conformation with  $C_{2v}$  symmetry. Upper left: p-orbital diagram, right:  $C_{2v}$  character table. Lower left: magnetic ( $m$ ) and electric ( $\mu$ ) transition dipole moment for the transition between the  $A_1$  ground state to the  $B_2$  excited state. Lower right: opposite helicities may be recognized when looking at the molecule from different angles.



associated with excitation of an electron from HOMO to LUMO. Here the molecule goes from the ground state with  $A_1$  symmetry to the  $B_1$  excited state. As can be seen from the group table, the transition is electric dipole allowed in the  $x$ -direction and magnetic dipole allowed in the  $y$ -direction. These two transition dipole moments can be decomposed into components along the  $-45^\circ$  and  $+45^\circ$  directions in the  $x,y$  plane. The electric ( $\mu$ ) and magnetic ( $m$ ) dipole components along the  $+45^\circ$  direction point in the same direction, indicating preferential emission of left polarized photons in directions perpendicular to  $+45^\circ$ . In contrast, the components of  $\mu$  and  $m$  in the  $-45^\circ$  direction are antiparallel corresponding to preferential emission of right circularly polarized light.

So in summary, for molecules belonging to the four achiral point groups in Table 1, one can find combinations of components of electric and magnetic transition dipoles that together transform as the totally symmetric representation such that circularly polarized emission is possible in particular emission directions. Yet when integrated over all directions, the circular polarization should cancel out completely. Only molecules with structure belonging to the chiral point groups will emit light with a net circular polarization when integrated over all angles.

### CPL from isolated small molecules

In recent decades synthetic chemistry has yielded many new luminescent chiral molecules. At the same time equipment for measuring circular polarization in luminescence has become far more widely available. This combination of events has led to numerous interesting studies regarding CPL. Here we first focus on studies involving well dispersed molecules of limited molecular weight.

For an ensemble of small, dispersed molecules in isotropic solution, the dissymmetry factor is predicted to be [Eq. (2)]:

$$g_{lum} = \frac{4c|\mu| \cdot |m| \cos \theta}{|\mu|^2 + c^2|m|^2} \quad (2)$$

Where  $\mu$  is the electric and  $m$  the magnetic transition dipole moment associated with the luminescent transition. Both transition dipoles are expressed in SI unit in this version of the equation. (The expression in cgs units  $g=4|\mu||m|\cos\theta/(\mu^2+m^2)$  is slightly simpler but has the disadvantage that electric and magnetic transition dipoles should be entered in cgs units, a system of units that is largely obsolete).  $\theta$  denotes the angle between these two transition dipole moments. The expression (2) is an approximation which neglects contributions from higher order moments of the transition charge density. Especially for larger structures such as aggregates and polymers, these neglected higher order transition moments may actually become more important.

A direct experimental test of relation 2 has not been undertaken so far, which is related to the complexity of optimizing the excited state in quantum chemical calculations.<sup>[69]</sup> For the reverse transition, from ground to

excited state, (2) should hold as well, provided that one computes the transition dipole moments for the ground state geometry. In this simpler case circumventing the need for excited state optimization, quantum theoretical predictions for the circular polarization can match the experimental results quite closely.<sup>[70,71]</sup>

Mori and coworkers have undertaken a systematic comparison between the dissymmetry factors in luminescence ( $g_{lum}$ ) and in absorption from the ground state to the lowest excited state ( $g_{abs}$ ).<sup>[72]</sup> A correlation between  $g_{abs}$  and  $g_{lum}$  is experimentally confirmed for a large dataset. Yet the general trend  $|g_{lum}| \leq |g_{abs}|$  indicates that geometric distortion and relaxation occurring in the excited state before photon emission often have a significant effect on  $g_{lum}$ .<sup>[73]</sup>

The relation between degree of circular polarization and magnetic and electric transition dipole moments, as expressed in (2), provides some insight into which molecules may approach the maximal circular polarization with  $|g_{lum}|=2$  in their luminescence. The argument starts by considering the magnitude of the magnetic transition dipole moment.

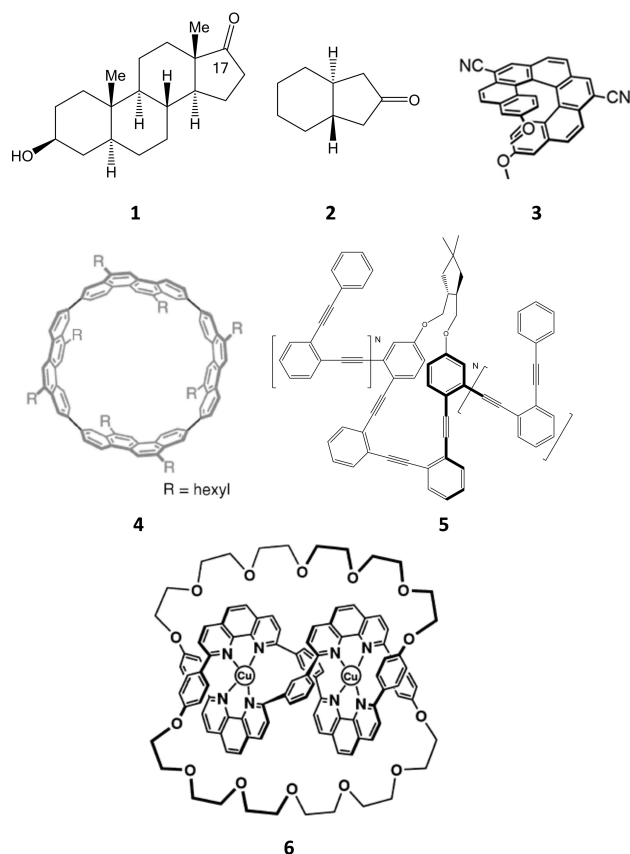
The magnetic moment obeys the dipole selection rule for the angular momentum quantum number  $\Delta L=0, \pm 1$ , not  $L=0 \leftrightarrow L'=0$ . Here for simplicity we have neglected any coupling between orbital and spin angular momentum.

Now because in molecules of low symmetry the orbital angular momentum of the electrons is usually quenched ( $\langle L \rangle \cong 0$ ) it follows that the magnitude of the magnetic transition dipole moment will in practice be limited to a few Bohr magnetons. Here the Bohr magneton is the atomic unit for magnetic moment, corresponding to the orbital magnetic moment of an electron with  $L=1$ , i.e. with an angular momentum equal to  $\hbar$ .

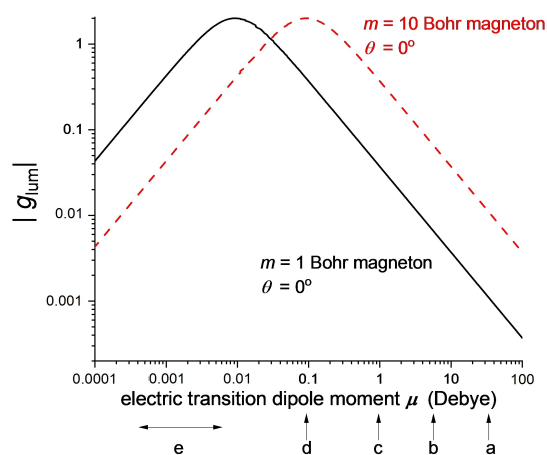
Spectroscopy with circularly polarized light is one of the few techniques that allows experimental access to the magnetic transition dipole moment. In Table 2, some experimental values for the magnetic transition dipole moment in absorption for the compounds in Scheme 1 are listed. The largest magnetic transition dipole moment known today amounts to some 10 Bohr magnetons for compound 4, and is enabled by the almost cylindrical symmetry of the molecule, see Scheme 1 and Table 2.

**Table 2.** Electric ( $m$ ) and magnetic ( $m$ ) transition dipole moments for spin-allowed transitions of various orbital nature in small molecules.

Molecule	Magnetic dipole moment (Bohr magneton)	Electric dipole moment (Debye)	Transition type <sup>1</sup>
1 <sup>[74]</sup>	1.0	0.16	$n-\pi^*$
2 <sup>[75,76]</sup>	1.2	0.14	$n-\pi^*$
3 <sup>[77]</sup>	2.6	2.7	$\pi-\pi^*$
4 <sup>[78]</sup>	10.9	1.25	$\pi-\pi^*$
5 <sup>[79]</sup>	4.7	5.2	$\pi-\pi^*$
6 <sup>[80]</sup>	0.5	2.8	MLCT
Cr(III) tris oxalate <sup>[81]</sup>	0.36	0.26	d-d ( ${}^4T_{2g} \rightarrow {}^4E_g$ )
Eu(III) <sup>[82-84]</sup>	0.2	Var.	f-f ( ${}^5D_0 \rightarrow {}^7F_1$ )
PbBr <sub>2</sub>	> 0.1	2	band-to-band
perovskite <sup>[85]</sup>			



**Scheme 1.** Molecular structure of some small molecules. Note that **6** is a divalent cation incorporating two Cu(II) ions.



**Figure 9.** Absolute magnitude for the luminescence dissymmetry factor  $g_{\text{lum}}$  as function of the magnitude of the electric transition dipole moment  $\mu$  according to Eq 2 assuming a magnetic transition dipole moment  $m$  of 1 Bohr magneton (black solid line) and perfectly parallel orientation of magnetic and electric transition dipole moments. The red dashed line shows results for  $m = 10$  Bohr magneton. For reference, electric dipole moments from some transitions are indicated on the x axis: a) bacteriochlorophyll  $Q_y$ ,<sup>[86]</sup> b) anthracene 250 nm band pol. || to the long axis, c) anthracene 365 nm band pol. || short axis,<sup>[87]</sup> d) cyclopentanone,<sup>[88]</sup> e) Eu(III)  $^5D_0 \rightarrow ^7F_1$ .

In Figure 9 we have plotted the absolute value of  $g_{\text{lum}}$  as function of the magnitude of the electric transition dipole moment, assuming a magnetic transition dipole moment of

1 Bohr magneton in the direction parallel to the electric dipole moment (black line). For completeness we also report the result for the largest magnetic transition dipole known today of 10 Bohr magnetons. As can be seen, the maximum  $g$  value is reached for very small electric transition dipole moments, in any case  $\mu < 1$  Debye. The maximum  $g$ -value results when  $c m = \mu$ . Thus for an allowed transition in a dye molecule with  $\mu > 5$  Debye, it is practically impossible to reach a degree of circular polarization above 5%.

The dissymmetry ratio  $g_{\text{lum}}$  of a luminescent molecule can be altered by the environment in which it is placed. For instance, near a reflecting metal surface, the electric field strength is suppressed by interference between the incoming and reflected light beam. In contrast, the magnetic field is locally enhanced. By placing a chiral molecule with  $|c m/\mu| < 1$  i.e. a suboptimal ratio of magnetic and electric dipole strength for strong circular polarization close to a metal surface, one can suppress the contribution of the electric dipole to the emission and absorption relative to that of the magnetic dipole. This can lead to an enhancement of  $g_{\text{lum}}$  as shown by Tang and Cohen.<sup>[89]</sup> At the same time however one expects a decrease in  $g_{\text{lum}}$  for molecules that already have the optimal ratio of magnetic and electric dipole strength. Therefore, the change in  $g_{\text{lum}}$  near a metal is not a general property of the modified optical field but varies with the chiroptical properties of the molecule at hand.

Luminescent molecules are now routinely applied in organic light emitting diodes. Obviously, the efficiency for generation of photons from these diodes depends on the quantum yield of luminescence from the molecules. For reducing the influence of unwanted reflection of ambient light by the display, circular polarization of the emission may be employed. Furthermore, the coming generation of displays may be stereographic and also here circular polarization of light offers opportunities. For these advanced applications one would need luminescent molecules that combine high  $g_{\text{lum}}$  with high  $\phi_{\text{lum}}$ . For organic molecules with high  $g_{\text{lum}}$  and thus low dipole strength, the rate for non-radiative decay is usually considerable, resulting in typically low values for the quantum yield of luminescence ( $\phi_{\text{lum}}$ ). The relation between  $g_{\text{lum}}$  and  $\phi_{\text{lum}}$  has recently been explored in detail for a wide range of new compounds,<sup>[90–93]</sup> also with the aim of assessing potential for technological application. New metrics have been introduced incorporating  $g_{\text{lum}}$  and  $\phi_{\text{lum}}$  to aid the search for optimized compounds.<sup>[94,95]</sup>

The efficiency of organic light emitting diodes can be improved by using luminescent molecules that allow for thermally active delayed fluorescence. In the diodes, excited states are created by recombination of negative (electrons) and positive (holes) charge carriers that are injected via the electrodes. Recombination of charge carriers with parallel spins results in a high fraction of excitations with triplet spin character rather than to the fluorescent singlet excited state. Thermally activated delayed fluorescence is a process by which triplet excited states convert spontaneously to singlet excited states with the help of thermal energy. In a light emitting diode this

conversion of triplets into fluorescent states boosts the overall efficiency of the display.

A number of studies have investigated the possibility to combine the thermal activation process of triplet states with the generation of circularly polarized fluorescence.<sup>[96–103]</sup> Indeed molecules have been found that combine these two functionalities, providing useful leads for the further development of display technology relying on organic molecules.

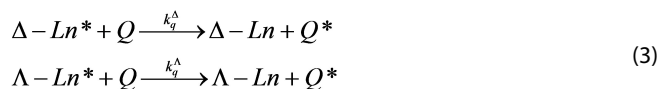
Trivalent lanthanide ions have interesting circular polarization of luminescence properties. In the visible and near infrared range, the spectroscopic transitions of the lanthanide ions involve the inner 4f shell. The electrons are shielded from the environment and can emit a photon with high quantum yield, especially for terbium(III) and europium(III).<sup>[104]</sup> In the free ion, the 4f–4f transitions are electric dipole forbidden but particular transitions can have large magnetic transition dipole moments. As a result, the magnetic dipole allowed transitions of the lanthanide ions can show strong circular polarization of luminescence.<sup>[105–108]</sup>

A most interesting case is the  $^5D_0 \rightarrow ^7F_1$  transition of the trivalent europium ion. For the bare ion, this transition is magnetic dipole allowed with  $m \cong 0.2$  Bohr magneton. Usually for this transition the magnetic dipole character predominates, as can be confirmed experimentally by measuring the linear polarization of this transition<sup>[109,110]</sup> or the interference pattern for the emission when embedded in a film.<sup>[111,112]</sup> If the Eu(III) ion is incorporated in a chelate with sufficiently low symmetry, the transition can acquire some electric dipole character. For the  $Cs[Eu((+)-hfbca)_4]$  complex in chloroform the balance between electric and magnetic dipole moment strikes about right resulting in one of the highest  $g_{lum}$  values ever reported: +1.38 at 595 nm.<sup>[113]</sup> Despite the low dipole strength for emission, the Eu(III) luminescence can be quite bright. Also for transition metal complexes with Cr(III), high  $g_{lum}$  sometimes combines with bright luminescence.<sup>[114–116]</sup>

The first coordination sphere of a lanthanide chelate is usually flexible which allows the lanthanides to be used as a dynamic probe.<sup>[117–120]</sup> The lanthanide ions may be complexed directly to the molecule of interest, for instance in studies of metal binding proteins<sup>[121,122]</sup> and nucleic acids.<sup>[123]</sup> Alternatively, one can also use specific lanthanide chelates to probe nucleic acids,<sup>[124–126]</sup> amino acids,<sup>[127–130]</sup> proteins<sup>[131,132]</sup> and sugars<sup>[133–135]</sup> In these studies one has to rely on relatively strong interaction of the lanthanide chelate with the analyte to induce some change in the transition probabilities of the lanthanide ion. Using lanthanide chelates one can also go one step further and probe even weaker binding events by making use of energy and/or electron transfer processes with the analyte. These transfer processes also modify the luminescence of the lanthanide ions but now there is no need for direct modification of the electronic structure of the luminescent lanthanide center in the ground state.<sup>[136,137]</sup>

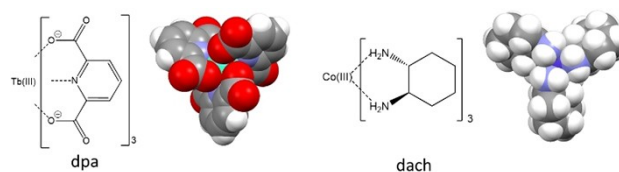
Formation of extremely labile, outer sphere complexes of lanthanide chelates with a wide variety of quencher molecules via diffusional encounter in liquid solution, suffices for efficient energy transfer from the photoexcited lanthanide chelate to the quencher. Rather surprisingly, it has been found that chiral

quencher molecules can show a remarkable enantioselectivity in their overall rate of quenching of the two mirror image related forms of the tris pyridine-2,6-dicarboxylate (dpa) chelates of Tb(III), Eu(III) and Dy(III) see Figure 10.<sup>[140,141]</sup> At room temperature the tris dpa chelates form a racemic mixture due to rapid racemization of the complex. The overall bimolecular rates for energy transfer between the  $\Delta$  and  $\Lambda$  optical isomers of the photoexcited lanthanide chelate and the chiral quencher Q may differ [Eq. 3]:

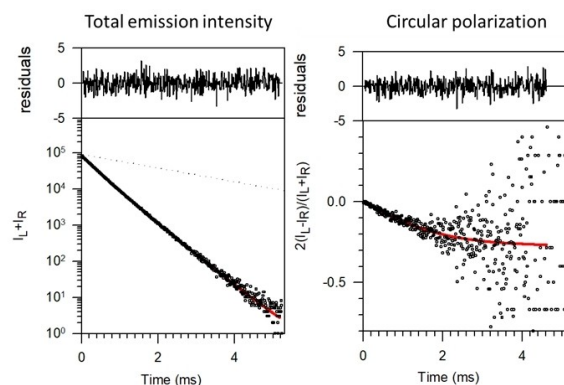


Time resolved circular polarization of luminescence spectroscopy has been instrumental in determining the enantioselectivity in these outer sphere energy transfer reactions.

The difference in the overall quenching rates of the  $\Delta$  and  $\Lambda$  forms of the photoexcited lanthanide chelate leads to a gradual enrichment of the excited state population in one of the two enantiomeric forms. Because of the very weak binding of the quencher to the lanthanide chelates, the ground state population remains racemic. This can be proven experimentally by time resolved measurement of the circular polarization of the lanthanide luminescence under short pulses of unpolarized excitation light, see Figure 11. Shortly after excitation the



**Figure 10.** Chemical structure of the pyridine-2,6-dicarboxylate (dpa) and trans (1*R*,2*R*)-1,2-diaminocyclohexane (dach) ligands together with the crystallographically determined structures of  $\Delta$ -Tb(dpa)<sub>3</sub><sup>3-</sup><sup>[138]</sup> and  $\Delta$ -( $\lambda\lambda\lambda$ )Co(dach)<sub>3</sub><sup>3+</sup><sup>[139]</sup>



**Figure 11.** Time-resolved circular polarization of luminescence of Tb(dpa)<sub>3</sub><sup>3-</sup> in water partially quenched by vitamin B<sub>12</sub> at 19  $\mu$ M concentration. The red lines show a fit of a kinetic model incorporating different quenching rate constants for the  $\Delta$  and  $\Lambda$  forms of the photoexcited lanthanide chelate. The dashed line in the left panel shows the emission decay trace in the absence of quencher.



excited state population is still racemic as evidenced by a degree of circular polarization indistinguishable from zero. With time after excitation, the enantiomeric excess in the excited state population increases as shown by a time dependent change in  $g_{lum}$ . At long times after the excitation pulse, the enantiomeric purity in the excited state nears completion and the  $g_{lum}$  value levels off. At the same time due to the low emission intensity at long times after excitation, the statistical uncertainty in the determination of  $g_{lum}$  increases.

The degree of enantioselectivity in the quenching,  $E_q$ , can be defined as [Eq. (4)]:

$$E_q = (k_q^\Delta - k_q^\Lambda) / (k_q^\Delta + k_q^\Lambda) \quad (4)$$

$E_q$  lies between  $-1$  and  $+1$ , with the boundary values describing a completely enantioselective energy transfer process.

A large variety of chiral molecules was found to discriminate between the two enantiomers of the lanthanide chelate when acting as acceptor in the energy transfer with the photoexcited lanthanide complex, see Table 3 for a selection.

The results for a homologous series of cobalt trans-1,2-diamine cyclohexane (dach) chelates,<sup>[142–151]</sup> clearly shows the sensitivity of the enantioselectivity to small structural changes in the quencher. Studies of quenching by  $\Delta$ -Ru(phen)<sub>3</sub><sup>2+</sup><sup>[152–158]</sup> showed opposite enantioselectivities of Ln(dpa)<sub>3</sub><sup>3-</sup> in water and methanol, indicating that also the solvation shell around the coordination complexes can play an important role in the molecular recognition. Enantioselective quenching is not restricted to small inorganic complexes: also organic dye molecules,<sup>[159]</sup> vitamin B<sub>12</sub> derivatives<sup>[160]</sup> and vitamin B<sub>12</sub> – protein complexes,<sup>[161]</sup> transition metal-nucleotide complexes<sup>[162,163]</sup> and metal organic complexes with topological chirality<sup>[164]</sup> show chiral discrimination. Also metalloproteins (c-type cytochromes,<sup>[165–167]</sup> blue copper proteins,<sup>[168]</sup> myoglobin, hemoglobin<sup>[169]</sup>) show selectivity in their quenching. For the

cytochrome c550 protein, a single site-directed mutation of a lysine into a glutamate residue leads to a strong reduction in  $E_q$ , see Table 3. This indicates that the lanthanide tris dpa complex has specific hydrogen bonding interactions with amino functionalities. The importance of hydrogen bonding interactions is supported by results for the capped Co(III)(dach)<sub>3</sub><sup>3+</sup> complexes, See Table 3. Capping the Co(dach)<sub>3</sub><sup>3+</sup> on only once face with an nitrogen atom replacing three protons (indicated in the table by –mc), leads to only a minor modification of the enantioselectivity. In contrast, capping the complex on both sides and thereby removing all possibility for forming intermolecular hydrogen bonds with the lanthanide chelate (–bc), results in a drastic reduction of  $E_q$ . Furthermore, enantioselective quenching studies and NMR paramagnetic shifts of vitamin B<sub>12</sub> (cyanocobalamine) have also indicated the importance of hydrogen bonding interactions of amide functionalities of the vitamin with the carboxylate groups of the lanthanide chelate in the chiral recognition of Ln(dpa)<sub>3</sub><sup>3-</sup>.<sup>[170]</sup>

Crystallographic studies of cocrystals of enantiomerically resolved tris ethylene-1,2-diamine trivalent cobalt and lanthanide tris dpa complexes confirm the formation of hydrogen bonds between the carboxylate groups of the dpa and the amino groups on the cobalt complex.<sup>[171,172]</sup> No enantiomeric resolution of the Ln(dpa)<sub>3</sub><sup>3-</sup> was found to occur, yet the  $\Delta$ -[Tb(dpa)<sub>3</sub>]<sup>3-</sup> and  $\Lambda$ -[Tb(dpa)<sub>3</sub>]<sup>3-</sup> occupy different sites in the crystal. Spectroscopic studies on the cocrystals revealed a double exponential decay of the luminescence indicating different rates of energy transfer between the  $\Delta$  and  $\Lambda$  form of the lanthanide and the Co(III) complex. Enantiomeric resolution of Ln(dpa)<sub>3</sub><sup>3-</sup> in crystallization was found to occur with a functionalized cage amine complex cation,  $\Delta$ -[Co((NO<sub>2</sub>)<sub>2</sub>sar)]<sup>3+</sup> (sar = sarcophagine = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane). Yet in this case direct H-bonding interactions between the cations and anions are surprisingly limited and the success of the resolution requires consideration of a variety of other factors.<sup>[168]</sup>

Crystallographic studies for Ln(dpa)<sub>3</sub><sup>3-</sup> with a variety of racemic cobalt polypyridyl complexes did not yield evidence for geometrically restrictive  $\pi$ -stacking between Ln and Co complexes. Water molecules were found to hydrogen bond to carboxylate-O atoms.<sup>[173]</sup> Paramagnetic NMR studies have been used to monitor the dynamic association between tris-dipicolinate lanthanide with complex molecules capable of hydrogen bonding such as vitamin B<sub>12</sub>,<sup>[117,174]</sup> vitamin B<sub>12ar</sub> oligopeptides<sup>[175]</sup> and proteins.<sup>[176,177]</sup> X-ray structure analysis of crystals of Tb(dpa)<sub>3</sub><sup>3-</sup> with 2,2',2''-nitrilotris(ethylammonium) as trivalent counterion confirm hydrogen bonding interactions with the ethylammonium groups mimicking e.g. protonated lysine side chains in proteins.<sup>[178]</sup>

Crystallography on hen egg-white lysozyme protein with Eu(dpa)<sub>3</sub><sup>3-</sup> as one of the counterions has revealed the presence of enantioselective binding sites on the surface of the protein. The binding sites comprise a positively charged arginine residue involved in hydrogen bonding.<sup>[179]</sup> The presence of such selective binding sites has also been confirmed for other proteins.<sup>[180,181]</sup> Lanthanide chelates thus seem versatile probes

**Table 3.** Enantioselectivity ( $E_q$ ) and average rate constant  $(k_q^\Delta + k_q^\Lambda)/2$  for quenching of Eu(dpa)<sub>3</sub><sup>3-</sup> luminescence by various quenchers in water at room temperature.<sup>[142,166]</sup>

Quencher		$E_q$	$(k_q^\Delta + k_q^\Lambda)/2$ $10^{-7} \times (M^{-1}s^{-1})$
Co(III)(dach) <sub>3</sub> <sup>3+</sup>	$\Delta$ -( $\lambda\lambda\lambda$ )	-0.56	7.6
	$\Delta$ -( $\lambda\lambda\lambda$ )-mc <sup>[b]</sup>	-0.60	5.6
	$\Delta$ -( $\lambda\lambda\lambda$ )-bc <sup>[c]</sup>	-0.23	2.8
	$\Delta$ -( $\lambda\lambda\delta$ )	+0.13	5.2
	$\Delta$ -( $\lambda\delta\delta$ )	+0.62	6.1
	$\Delta$ -( $\delta\delta\delta$ )	+0.74	1.8
Cytochrome c	horse	+0.48	7.5
	cow	+0.48	
	chicken	+0.45	
	pigeon	+0.44	
	Tuna	+0.20	(7.5) <sup>[d]</sup>
Cytochrome c <sub>550</sub> <sup>[a]</sup>	wild type	+0.20	7.6
	Lys14→Glu	+0.22	2.3
	Lys99→Glu	+0.10	1.7

[a] from *Paracoccus versutus*. [b] mono-capped derivative with protons of three amino group on one face replaced by a-N = moiety [c] bi-capped [d] Calculated assuming the same extinction coefficient as for the protein from horse.

for biomolecules. The lanthanide complexes can act as phasing agents when using anomalous diffraction to help solve the structure of the proteins.<sup>[182–185]</sup> Moreover lanthanide complexes derived from the pyridine carboxylate can be used as nucleating agents<sup>[186]</sup> and to consolidate protein–protein interfaces.<sup>[187]</sup>

We end this section of circularly polarized luminescence from isolated molecules by reviewing the first pioneering studies towards detection of circular polarization from a single molecule.<sup>[188,189]</sup> These studies are challenging because molecular structures that have large degree of circular polarization generally have low dipole strength. The low dipole strength implies either low quantum yield for luminescence or long excited state lifetimes, both of which are detrimental for single molecule spectroscopy. Furthermore, single molecules are often studied under conditions where free molecular tumbling is impaired and hence the isotropic limit with effective averaging over all molecular orientations is difficult to achieve. The degree of circular polarization is actually a tensorial quantity that can vary strongly depending on the direction of propagation of the photon.<sup>[190–193]</sup> Hence degrees of circular polarization from immobile molecules differ considerably from the results in solution.<sup>[194]</sup> In fact it has been realized early on that anisotropy can play a role in CPL measurements especially under where photoselection in excitation occurs and where tumbling is slow.<sup>[195]</sup> Finally, as we have discussed earlier, even achiral molecules may emit circularly polarized photons in specific direction. This illustrates the difficulty of realizing reliable control experiments in which circular polarization is fully absent. Nevertheless, polarization spectroscopy on single emitters in close proximity to metal nanostructures will most likely become an important new direction.<sup>[196]</sup>

### Aggregates of molecules

For many chiral molecules, circular polarization of their luminescence only becomes apparent upon aggregation of the molecules.<sup>[197–200]</sup> The reasons for this intriguing induction of CPL can be many.

First, when chromophores of different type co-assemble into an aggregate, new electronic states and associated spectroscopic transition may arise that do not exist in the separate components. A well-known example is the formation of charge transfer excited states and the associated charge transfer luminescence.<sup>[201,202]</sup>

A second contributing factor to the emergent circular polarization is that some chromophores have vanishingly low quantum yield for luminescence when present as isolated dissolved species and only become luminescent upon aggregation.<sup>[203–205]</sup> This aggregation induced emission can often be attributed to a suppression of non-radiative decay involving torsional motion of the  $\pi$ -system.<sup>[206]</sup>

Finally, and most importantly, many chiral chromophoric molecules feature a flat system of  $\pi$ -electrons featuring high local symmetry with the stereocenters being present in an aliphatic side chain. The remoteness of stereocenters from the

active chromophoric part then often results in a perturbation of the  $\pi$  electrons that is not strong enough to induce sufficient electric and magnetic character in the transition to give rise to measurable circular polarization. Yet when two or more such molecules aggregate the stereocenters may impose a chiral arrangement so that the electric transition dipole moments can couple. The coupled motion of the oscillators can now have circular component and hence the transition acquires also magnetic dipole character and becomes CPL active.

The exciton coupling of locally achiral chromophores that are covalently attached to a chiral scaffold, have been studied extensively by Nakanishi and coworkers providing the basis of the exciton chirality method for determining absolute chirality.<sup>[207]</sup>

Advances in supramolecular chemistry in recent decades now make it possible to bring multiple chromophores together with a controlled geometry without the need for covalent bonds between the dyes.<sup>[208,209]</sup> Also with the supramolecular interactions the exciton coupling will induce circular polarization. In this fashion also circular polarization can be induced in the emission of achiral chromophores.<sup>[210–213]</sup>

So delocalization of the electronic excitation over more than one molecule in a supramolecular aggregates can induce circular polarization of the luminescence. This naturally raises the question what the actual spatial extent of this delocalization might be. While electronic coupling between the molecules favors delocalization of the excitation, there are also several factors that limit the extent of delocalization. First, disorder in the aggregate favors localization. If disorder is present in the structure, some molecules will have a lower excitation energy than others and naturally the electronic excitation will, after relaxation, tend to localize near the molecule with the lowest excitation energy. A second counterforce to delocalization is provided by molecular vibrations. In many  $\pi$ -conjugated molecules the electronically excited chromophore can lower its energy by changing its nuclear coordinates. For example, in  $\pi$ -systems with alternating single and double bonds there is often a partial reversal of the bond length alternation<sup>[214]</sup> upon electronic excitation. In the lowest electronic excited state, carbon-carbon bonds within the system that are relatively short in the ground state become slightly longer in the excited state.<sup>[215]</sup> The energy released upon the geometric relaxation is maximal when the excitation is localized on a single chromophoric group. Delocalization of the excitation suppresses the relaxation associated with the nuclear rearrangement.<sup>[216,217]</sup>

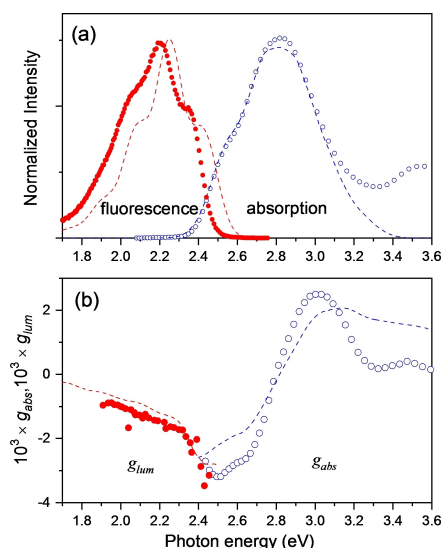
Quantum theoretical studies predict that the exciton delocalization couples with zero-point vibrational motion of the nuclei in the excited state, resulting in so-called dynamic localization of the exciton.<sup>[218,219]</sup> Here the degree of electronic delocalization changes – the exciton “breathes” – during the cycle of zero-point vibrational motion.<sup>[220]</sup> The dynamic localization of an exciton in a chiral molecular aggregate can lead to a degree of circular polarization that varies across the emission band, approaching zero for the higher vibronic transitions at the long wavelength tail of the band.<sup>[221]</sup> The dynamic local-

ization is associated with breakdown of the Born-Oppenheimer approximation. The structure and the nuclear vibrations of the molecule are no longer independent of the motion of the electrons.

Attempts to verify these theoretical predictions experimentally have focused on chiral coherent nonlinear spectroscopy on light harvesting complexes in photosynthesis<sup>[222,223]</sup> and on circular polarization of luminescence on synthetic chiral supramolecular aggregates. The latter we will discuss further in this review.

In Figure 12, the top part shows the fluorescence and absorption spectrum of supramolecular aggregates of oligophenylvinylene (OPV) molecules in solution. The lower part show the corresponding degree of circular polarization in fluorescence and in absorption. What is immediately clear from these measurement is that the dissymmetry ratio  $g_{lum}$  is not constant throughout the fluorescence band. An explanation of the circular polarization in terms of one electric and one magnetic transition dipole moment will not give a satisfactory explanation, because according to Eq. 2 the two moments should give constant  $g_{lum}$ . The wavelength dependence of  $g_{lum}$  and also  $g_{abs}$  could be modelled including electronic coupling between the molecules, variation in the excitation energy of the molecules due to disorder and dynamic localization of the excitation as the result of vibrational motion in the excited state. The spectral properties can be described by a Gaussian distribution of excitation energies with a width  $\sigma=0.12$  eV and a spatial correlation length  $l_0 \approx 5$  molecules. Disorder and vibrational motion in the excited state localize the excitation, such that it is coherent over only 2–3 molecules.<sup>[224,225]</sup>

The wavelength dependence of the degree of circular polarization has also been observed for other systems of coupled chromophores<sup>[226,227]</sup> and often poses a challenge when interpreting CPL spectra.<sup>[228]</sup>



**Figure 12.** a) Experimental absorption and fluorescence spectra of MOPV4 helices taken at 278 K b) Corresponding degrees of circular polarization in absorption and luminescence. Also shown as dashed curves are theoretical spectra based on the disordered Holstein Hamiltonian.<sup>[220]</sup>

Finally, to conclude this section on nanostructure, we note that supramolecular chemistry has now advanced to a level where shape-persistent, functional microstructures can be synthesized and studied at the single particle level. In these synthetic structures the angle dependence or anisotropy of circular polarization of the luminescence has been measured for single particles.<sup>[229]</sup> This CPL anisotropy method may become instrumental to studying the inner structure of nano objects, perhaps evolving into a form of optical tomography.

## Materials

After having discussed isolated molecules and molecular aggregates, we now turn our attention to molecular materials. Completely circularly polarized luminescence from condensed matter is an objective that is of practical importance in display technology. In the past decade, it has become clear that the goal of electrically powered, completely circularly polarized light emission with molecular materials as active layer is essentially within reach. Yet, to date, the first technological application has not appeared, although it might be imminent.

Here we break down the developments in two steps. First, we discuss circularly polarized photoluminescence with high  $g_{lum}$  value from molecular solids. Then, we turn to electroluminescence with circular polarization.

Inorganic semiconducting crystals with chiral structure featuring circularly polarized light emission are extremely rare, although the latest research on lead halide perovskites is yielding examples.<sup>[82,230,231]</sup> In contrast cholesteric liquid crystals offer materials with highly tunable structure featuring large circular polarization effects. In a landmark publication in 1999, Shaw Chen and coworkers showed how the polarization of photoluminescence from a molecular solid with cholesteric organization can be tuned systematically to achieve almost complete circular polarization.<sup>[7]</sup> The system developed involves achiral molecular fluorophores embedded in a chiral nematic host. In subsequent investigations, Chen et al. showed<sup>[232]</sup> that the circular polarization can be modeled quite accurately building on the Oseen-Mauguin-DeVries theory<sup>[233,234]</sup> for the optical properties of the cholesteric host. In essence the circular polarization is not generated locally at the site of photon emission, but arises as the light travels through the host out of the material. The circular polarization attained critically depends on macroscopic quantities such as e.g. the thickness of the film.

The absorption bands of chromophores embedded in a cholesteric host materials can show particularly large degrees of circular polarization.<sup>[235–239]</sup> Also the luminescence of achiral fluorophores in a chiral host can acquire circular polarization.<sup>[240–244]</sup>

The next step in this development came with fluorescent molecules that by themselves can adopt a chiral nematic organization. In particular, so called rigid-rod polymers with sidechains bearing enantiopure stereocenters such as polyfluorene<sup>[245–247]</sup> and polyphenylethynylene<sup>[248]</sup> can adopt



chiral nematic phases. Upon rapid cooling, the cholesteric molecular order can be vitrified and the remarkable chiroptical properties of cholesteric liquid crystal phase are largely retained by the solid film. Fluorescent  $\pi$ -conjugated polymers can also be ordered using a chiral nematic liquid crystal host to induced high circular polarization.<sup>[249–252]</sup> Also lyotropic chiral nematic phases can be used to induce large degrees of circular polarization.<sup>[253]</sup>

For technological applications, circularly polarized photoluminescence is less relevant. In the last decades it has become clear that molecular materials can very efficiently yield photons from recombination of positive and negative charge carriers injected into the material via electrical contacts. Such electroluminescence can be circularly polarized. The first measurements of this effect<sup>[44]</sup> were still solution based. Also, from molecular solids the effect could be proven.<sup>[254]</sup> The degree of circular polarization can be boosted through thermal annealing of polymeric materials that have a chiral nematic phase at elevated temperature.<sup>[242,255–257]</sup> Alternatively, also light emitting materials with spin forbidden transitions can yield light emitting diodes with high degree of circular polarization.<sup>[258–260]</sup>

Altogether a very rich research field has emerged at the boundary between chemistry and physics with plenty of opportunity for material design, theory, experiment and applications.<sup>[261,262]</sup> In latest developments, supramolecular interactions are used to tune the circular polarization of luminophores in liquid crystal host.<sup>[263–270]</sup> Furthermore, apart from the bottom-up approach to organization of functional materials starting from molecular chirality, also the top-down method seems a viable option: circular polarization can also be induced through macroscopic ordering.<sup>[271–273]</sup> Finally, we note that next to layers with static polarization characteristics, an important new development involves materials with (photo-) programmable or stimuli responsive chiroptical properties.<sup>[274–279]</sup>

## Discussion

In this section we discuss the paradoxes associated with circular polarization as presented in the theory section in relation to the progress in measurement techniques as well as in molecules and molecular systems with high circular polarization.

### Paradox I

As the first paradox we faced the question how a photon travelling at the speed of light could distinguish between the two mirror-image related forms of a molecule. A way out of this conundrum is by saying that selective emission or absorption of circularly polarized light cannot be described by a single space-time event. The emission or absorption of a linearly polarized photon by a hydrogen atom could in first approximation be described as a single space-time event: at a certain

moment in a time and at a specific position, an electron jumps from a higher energy Bohr-like orbital to a lower one and a photon is emitted. Here the dipole approximation is quite accurate, the spatial extent of the hydrogen atom in its lower electronic states is indeed small compared to the wavelength of light. For describing the circular polarization in the transition of a chiral molecule, the dipole approximation is no longer accurate. The electro-magnetic fields of the light wave can no longer be considered as constant over the volume occupied by the molecule. To bring out this sensitivity towards the shape of the wave, one needs at least two interactions between the electrons of the molecules and the electromagnetic fields. After all, chirality is a non-local geometrical property.

The chiral quantum of energy will have to interact at least twice with the chiral molecule to give rise to circular dichroism and circular polarization of luminescence. Indeed, in the exciton coupling model, the chiral molecule has to be modelled by at least two interacting chromophoric moieties to explain the circular selective absorption and emission of light. Furthermore, the minimal requirement of two space-time events also makes understandable why circular polarizers do not exist as single component optical element. Circular polarizers are made of two parts, a selective retarder (quarter wave plate) and a polarizer. The two components are required because we need at least two moments of interaction of the circular polarizer with the photon.

Thus, in the preferential emission of a photon with, say, right circular polarization, there will be at least two moments of interaction between the quantum of energy and the molecule. These two space-time events will not be fully independent but must influence in a manner dictated by the handedness of the molecule. In case of a bichromophoric compound the minimal two events required for the optical activity can be identified with interaction of the light with the two chromophores.

If we want to describe the relation between these two events, we will need to introduce a Hamiltonian or Lagrangian to describe the dynamics of the radiation-molecule system. According to (quantum-) field theory, different ways of description are possible depending on how we gauge the electromagnetic potentials involved in the potential energy term of the Hamiltonian or Lagrangian. A well-known option is the so-called Coulomb gauge, where one treats the electrostatic interaction among the electrons and nuclei in the molecule as instantaneous. At first sight, this seems to violate the requirement that no electromagnetic signal can travel faster than light. Yet it can be shown that if one properly accounts for all perturbation terms in the interaction of the molecule with the electromagnetic radiation, then it is possible to be fully compliant with the requirements of special relativity.

The other commonly used way to gauge potentials is the Lorenz gauge. Here electromagnetic interactions between different parts of the molecule are fully retarded and take place via the radiation field.

All quantum mechanical software involves the Coulomb gauge. In the exciton coupling model for circular polarization in chiral bichromophoric compounds, the photoexcitation of the

molecule changes the electron distribution on the two chromophoric units at exactly the same moment.

In the traditional description of the interaction of cholesteric liquid crystals with light, the spatially separated parts of the material couple via retarded interactions mediated via the electromagnetic field. In effect, this follows the Lorenz gauge description, with the details of the molecular quantum mechanics approximated by dielectric response functions and the laws of optics.

We still face the challenge of a simple and efficient description of the circular polarization in the spectroscopic transitions of chiral mesoscopic objects, viz. chiral supramolecular aggregates. Should we follow the molecular approach and compute electric and magnetic transition dipoles for the aggregate as a whole or should we follow the materials description, determine local electric polarizabilities and solve the wave equation for the internal electromagnetic fields? We have now learned that the difference in these two approaches stems from a choice in how we describe potentials. Both approaches, Coulomb or Lorenz gauge, are viable. In fact, in quantum field theories one often switches between various gauges looking for the most effective and efficient way to compute the desired quantity. It seems that also for intermediate sized molecular objects, we could follow such an approach. Then we will have to acknowledge that molecular quantum mechanics as we know it now is only an approximation. Similarly, mesogens are more than just polarizable ellipsoids: they have an internal electronic structure that can make all the difference.

## Paradox II

This paradox questions the assignment of left and right circular polarization to light wave not propagating in vacuum but through a medium. Light waves inside a molecular solid are complex phenomena. The picture where a circularly polarized light wave inside a medium is essentially the same as the wave in vacuum, but now travelling at a different speed  $c/n$  is untenable. To illustrate this we note that the eigen polarizations of light travelling through a cholesteric material are not purely circularly polarization, but rather undulate between elliptical polarizations.<sup>[234]</sup>

For resolving the second paradox, we can take advantage of understanding developed in quantum field theory. Massless particles travelling at the speed of light can only have two polarization states. For gravitational waves only two polarizations can be found. For the photon with spin  $S=1$  in vacuum, we have two independent polarizations, e.g., with clockwise and anticlockwise angular momentum. Yet for particles travelling at speed less than  $c$  with spin quantum number  $S=1$ , three different polarizations are possible.<sup>[280]</sup> This may also apply to light waves in a medium. Next to the two circular polarizations that we are so familiar with there must now be an additional polarization component. Here the choice of gauge matters. For Coulomb gauge, the extra component of the electromagnetic waves takes the shape of

a non-zero, time dependent electrical potential. For Lorenz gauge, the extra polarization component is in the direction of the propagation of the electromagnetic field: longitudinal polarization. While these additional polarization components by themselves play an insignificant role, the longitudinal waves for instance do not contribute to the energy density of the electromagnetic field, they do play a crucial role at the interfaces between different media. With regards to the problem of circular polarization in the spectroscopic properties of large chiral supramolecular structure, it seems obvious that scattering of light by these mesoscopic objects will be important. In contrast, for isolated molecules and bulk solids light scattering plays only a minor role. A proper account of circular selectivity in the scattering will require evaluation of boundary conditions for the electromagnetic fields. Here the additional polarization components of the electromagnetic waves that are possible in the denser media require closer attention. In fact, this problem of proper formulation of boundary conditions has been recognized also in the wider field of spectroscopy of solids and is known as the problem of the additional boundary conditions.<sup>[281]</sup> Finally to further illustrate the need for a deeper understanding of the generation of circular polarization in mesoscopic molecular object we mention that according to Cowieson et al., the circular dichroism of proteins can be influenced by protein-protein aggregation without the apparent changes in the secondary structure of the protein.<sup>[282]</sup> Hence circular polarization measurements hold information on the quaternary structure of a protein which may be highly significant for understanding biological function. Similarly also for nucleic acids it is known that higher order organization leads to significant changes in its circular dichroism spectra.<sup>[283,284]</sup>

## Paradox III

Can molecular structure be the ultimate answer to our questions regarding the origin of the circular polarization of molecular luminescence? The answer is probably no. For this I list the following reasons.

Molecular structure may be considered an emergent phenomenon.<sup>[285–287]</sup> The Hamiltonian for most molecules will feature many conformations with low energy. Which of these conformations is the relevant one in a particular experimental setting, depends on the interactions of the molecule with its environment with the history of the molecule playing a major role. In a spectroscopic experiment, we change environment of the molecules from dark to light. In general, the molecule will respond dynamically and so a static molecular structure can only be part of the complete answer.<sup>[288,289]</sup>

We have seen that wavelength dependent variations in the degree of circular polarization of molecular aggregates provide an important clue to the dynamics of the molecular response. The variation of the dissymmetry factor for the various vibronic side bands provides information on the coupling between electronic and vibrational degrees of freedom in the structure. Here one goes beyond the Born-Oppenheimer approximation,

and one leaves behind the idea of a molecular structure that is fully independent of the motion of the electrons during the spectroscopic transition. In a sense, this illustrates the relevance of the paradox.

Experimental and theoretical methods to study the influence of the dynamic coupling between electrons and nuclei are just emerging.<sup>[290]</sup> Further development of experiment techniques for circular polarization measurement with high spectral resolution<sup>[291]</sup> and ultrafast time resolution<sup>[292,293]</sup> may allow us to follow the dynamics of the molecules in more detail either Fourier transformed in the spectral domain or resolved in real time.

## Conclusion

In the past half century, circular polarization of luminescence has become firmly established as probe for small molecules in solution. In particular, the circular polarization may be used to study dynamic process such as molecular chiral recognition. Circular polarization in electrogenerated light emission from chiral molecular semiconducting materials can be significant and may have technological applications.

Circular polarization of luminescence is itself a quantum electrodynamicical phenomenon. Yet a detailed and comprehensive understanding including all relevant length scales is still a formidable and daunting task. If one is primarily focused on chirality at the molecular level aiming to determine for instance the absolute configuration of a molecule, then the often large circular polarization effects arising from supramolecular aggregation of the molecule of interest are pernicious artifacts that can easily destroy the reliability of the method. Conversely if one would like to understand the transmission of light through transparent materials with helical organization then forbidden transitions with their magnetic transition dipole moments are hardly of any relevance and had better be ignored. It seems likely that early pioneers in the field such as Lorentz, Emeis, Oosterhoff and Dekkers had fathomed this difficulty. The possibility of contributions to the circular polarization from helical organization at different length scales each with its own helicity seems to have been a major hurdle in establishing the circular polarization techniques and is probably still a cause of confusion between different subdisciplines.

In the description of an isolated electron interacting with electromagnetic fields, similar problems associated with different length and energy scales occur. Here one develops the interaction between electron and field in perturbation series which can ultimately be made to converge.<sup>[294]</sup> This indicates that a complete description of circular polarization effects in the interaction between molecular material and light may be possible. It may be that proper coarse graining of the problem using optics to describe the propagation of light through the medium at longer length scales and molecular quantum mechanics to deal with interaction of a local scale could provide an efficient and effective description. Solving this problem will have a major impact on optical tomography of chiral structures at the submicron length scale.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** circular polarization of luminescence · excited states · liquid crystals · molecular aggregates · molecular luminescence

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