Check for updates

Chemistry
Europe
European Chemical
Societies Publishing

Special
Collection

Chiral Chromium(III) Complexes as Promising Candidates for Circularly Polarized Luminescence

Maxime Poncet,[a] Amina Benchohra,*[a] Juan-Ramón Jiménez,*[a, b] and Claude Piguet*[a]

The search for chiral chromophores with efficient circularly polarized luminescence (CPL) is an on-going hot topic in chemistry due to their potential applications in emerging fields such as spintronics and photonics. Beyond the largely exploited p-block, 4d/5d-block and f-block chiral entities, chiral chromium (III) complexes have recently attracted interest because of the abundancy of chromium in the earth's crust, its kinetic inertness and its promising metal-centered $Cr(^2E)$ and $Cr(^2T_1)$ phosphorescence. The associated spin-flip transitions could provide large dissymmetric factor (g_{lum}) and high luminescence quantum yields (ϕ) when six-membered strong-field chelate rings are coordinated to chiral six-coordinate Cr(III) centers. In this minireview, we intend to focus our attention on the state-of-the-art for the design of pseudo-octahedral chiral mononuclear Cr(III) complexes for which chiroptical properties were investigated. The promising electronic properties of these complexes together with their low cost make these underexplored systems appealing candidates for CPL applications.

1. Introduction

Circularly Polarized Luminescence (CPL), which is the emission of polarized light with a certain degree of handedness from a chiral luminophore upon non-polarized light excitation, has attracted the attention of chemists and physicists since 1948 when Samoilov observed this phenomenon in a crystal of sodium uranyl acetate.[1] Later, Oosterhof and Emeis reported the first CPL measurements recorded in solution for a trans-β-hydrindanone chromophore and for the coordination complex $[Cr(en)_3]^{3+}$ (en=ethylenediamine).[2] Currently, the research devoted to CPL is boosted by the need for chiroptical features in a wide range of applications which spans from technological (security inks, CP-OLED)[3] to biological applications (molecular probes, bioimaging, chiral recognition).[4]

Major activity in the field of CPL has been focused on the development of chiral chromophores such as organic dyes,[5] 4d and 5d metal complexes,[5a,b] lanthanides-based complexes[6] and more sophisticated supramolecular/macromolecular architectures.[7] The latter approach seems to emerge as a novel strategy for enhancing g_{lum} in organic systems[8] because efficient CPL emitters require large dissymmetry factors (g_{lum}) and high quantum yields (ϕ).[5d] The first parameter is related to the degree of "enantiorichness" of the circularly polarized light emitted from a chiral chromophore and it can, theoretically, reach values of -2 or 2 when either pure right- or left-handed polarized light is emitted after standard excitation (Equation 1 with $I_R=0$ or $I_L=0$, see section 3). The second parameter, i.e. the quantum yield ϕ, states that the ratio of emitted over absorbed photons should be also maximized. As it is regularly reminded, chiral organic chromophores as well as 4d and 5d metal complexes are not good candidates for enhancing the dissymmetry factors due to the electric-dipole allowed character of their electronic transitions.[6b] However, they usually show high quantum yields arising from intense metal-to-ligand charge transfer or ligand-to-metal charge transfer and $\pi^*\rightarrow\pi$ transitions, which can compensate somehow their low g_{lum}. In addition, their considerable kinetic inertness makes those systems still attractive candidates for applications.

In this context, the maximization of g_{lum} in a chiral molecule requires the operation of electrically forbidden and magnetically allowed electronic transitions (Equation 2, see section 3), a situation encountered for intrashell f-f and d-d transitions in the free ions.[9] Transposed to molecular systems, the success of these predictions can be mainly assessed in lanthanide-containing complexes where the crystal-field effects are minimized with the establishment of the current record value of $g_{lum}=+1.38$ at 595 nm for $Cs[Eu[(+)\text{-}(hfbc)_4]$ (hfbc=(+)-3-heptafluorobutylyryl-camphorato) in solution at room temperature.[10] However, the high cost for the extraction and purification or rare earth together with their intrinsic kinetic lability are not negligible shortcomings for potential applications. Currently, the research of photoactive molecules based on earth-abundant metals (basically first-row 3d-block metals) is an emerging area because they represent a realistic alternative to precious metals (Ru, Ir, Pt or Au) and to lanthanides within the context of energy conversion.[11] How-

[a] M. Poncet, Dr. A. Benchohra, Dr. J.-R. Jiménez, Prof. C. Piguet
Department of Inorganic and Analytical Chemistry
University of Geneva
Quai E. Ansermet 30, 1211 Geneva 4 (Switzerland)
E-mail: Amina.Benchohra@unige.ch
jrjimenez@ugr.es
Claude.Piguet@unige.ch
[b] Dr. J.-R. Jiménez
Department of Inorganic Chemistry
University of Granada
Unidad de Excelencia en Química (UEQ)
Avda. Fuentenueva S/N, 18071, Granada (Spain)

These are not the final page numbers! ↗↗

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

**Chemistry
Europe**

European Chemical
Societies Publishing

ever, the lack of emissive states in 3d metal based complexes due to their limited ligand field strength have restricted their use in the field of photochemistry although much efforts are being devoted to overcome this limitation.[12] Together with the development of those cheap photoactive molecules, we and others started to exploit the intrinsic nature of the d-d transitions in the context of CPL. Since the development of the ruby laser by Maiman,[13] Cr(III) complexes are indeed among the most investigated coordination complexes in photophysics. Because of their kinetic inertness (large crystal field stabilization energy for the d^3 electronic configuration)[14] and their sharp NIR electric-dipole (Laporte) and spin forbidden $Cr(^2E \rightarrow {}^4A_2)$ and $Cr(^2T_1 \rightarrow {}^4A_2)$ emissions when embedded into strong ligand field environments ($\Delta/B \geq 20$ in the associated Tanabe-Sugano diagram),[13–14,15] these metal complexes open new avenues for the development of CPL emitters based on cheap metals.[16]

This minireview reports on the chiral Cr(III) complexes, for which the chiroptical properties were recorded and discussed.

2. Chirality of Cr(III) Complexes

General chirality definition relates to the geometric property of an object of not being superimposable with its mirror image. The genesis of chirality drew on the outstanding development of stereochemistry, energized by Le Bel[17] and van't Hoff[18] in the organic field and extended in the inorganic domain by Werner[19] at the end of the 19th century. However, it was not until a century later, in 1966, that its formalization was established by Cahn, Ingold and Prelog (CIP).[20] The renowned trio defined a clear-cut classification structure accounting for the several chirality types, notably those that did not originate from a tetrahedral carbon. Thus, the CIP rules are now common use to determine molecules configuration and describe the possible chirality encountered in organic chemistry and coordination chemistry, i.e. central chirality, planar chirality, helical chirality and axial chirality. Admittedly, the understanding of the stereochemistry deviating from organic systems harboured greater complexity (than carbon's one) and was thus deferred. Nevertheless, the d-block is an undeniable source of compounds featuring multi-faceted chirality.[21] Chiral mononuclear Cr(III) complexes noticeably demonstrate it, with chirality induced by the wrapping of chelates around the metal center (Δ/Λ helicity), chiral ligands (R/S), or by the ligand conformation within individual rings (δ/λ).

Prior to analyze these systems, it may be convenient to specify chirality from a symmetry-oriented perspective. To be chiral, a molecule must have a symmetry devoid of improper symmetry elements (i.e. inversion center, reflective planes, rotation-reflection axes). Interestingly, chirality was originally termed *dissymmetry* by Pasteur who remarkably suspected the crystal dissymmetry as a result of a dissymmetry at the molecular level.[22] It is also worth noting that it should not be confused with *asymmetry*-referring to the absence of symmetry elements (except the identity E). To observe this rule experimentally and access chiral complexes, chemists can adapt their design while tuning ligand denticities, flexibilities, symmetries

as well as coordination modes. A general description of these points is outlined below for selected Cr(III) compounds containing: (i) achiral planar ligands, (ii) stereogenic ligands and (iii) achiral flexible ligands inducing chirality upon complexation. Readers interested in further details are referred to corresponding literature.[21,23]

2.1. Helical Chirality

2.1.1. Monodentate Ligands

First, the arrangement of six monodentate ligands A around the metal in $[CrA_6]$ leads to the highest accessible symmetry O_h, which is achiral. The successive replacements of A with different B ligands exclusively lead to the formation of achiral compounds with reduced-symmetry. Each heteroleptic complex $[CrA_4B_2]$ and $[CrA_3B_3]$ has two geometrical isomers, cisoid (*cis*) and transoid (*trans*) in the former case and facial (*fac*) and meridional (*mer*) for the latter. It is only the distribution of at least three different monodentate ligands (A, B and C) about the metal center in $[CrA_xB_yC_{6-x-y}]$ that enables the emergence of chirality of central kind. However, examples of this type are very limited, likely due to synthetic challenges.

2.1.2. Didentate Ligands

On their side, didentate chelates are one of the most often encountered sources of chirality in coordination chemistry (Figure 1a). Bis and tris-(chelate) complexes display a helicity (Δ or Λ) associated with the trigonal twist of the ligands. The highest chiral symmetry D_3 is attained with homoleptic tris-chelate $[Cr(A^\cap A)_3]$ complexes, where $A^\cap A$ is a symmetrical didentate chelating ligand such as the archetypal bipyridine, phenanthroline or oxalate. The number of geometrical isomers increases when using unsymmetrical ligands $A^\cap A'$ as illustrated for the chiral $[Cr(A^\cap A')_3]$ complex, which can exist as a C_3-symmetrical *fac*-isomer or a C_1-symmetrical *mer*-isomer (Figure 1a top). Further complications arise for heteroleptic tris-chelate complexes where $[Cr(A^\cap A)_2(B^\cap B)]$ indeed corresponds to a single chiral isomer (Figure 1a bottom), but $[Cr(A^\cap A')_2(B^\cap B)]$ provides three different chiral isomers. Naturally, related analyses hold for the bis-chelate complexes $[Cr(A^\cap A)_2B_2]$, which can exist as a chiral *cis*-$[Cr(A^\cap A)_2B_2]$ isomer with C_2-symmetry or as an alternative achiral *trans*-$[Cr(A^\cap A)_2B_2]$ isomer with D_{2h} symmetry (Figure 1a bottom).

2.1.3. Tridendate Ligands

Contrary to didentate ligands, tridentate planar ligands provide fewer opportunities to achieve chiral complexes (Figure 1b). For instance, the famous homoleptic bis(terpyridine) chromium (III) $[Cr(tpy)_2]^{3+}$ complex adopts the achiral D_{2d}-symmetrical $[Cr(mer-A^\cap A'^\cap A)_2]$ arrangement[24] and the exceptionally luminescent $[Cr(tpe)_2]^{3+}$ complex (tpe is the tripodal ligand 1,1,1-tris

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
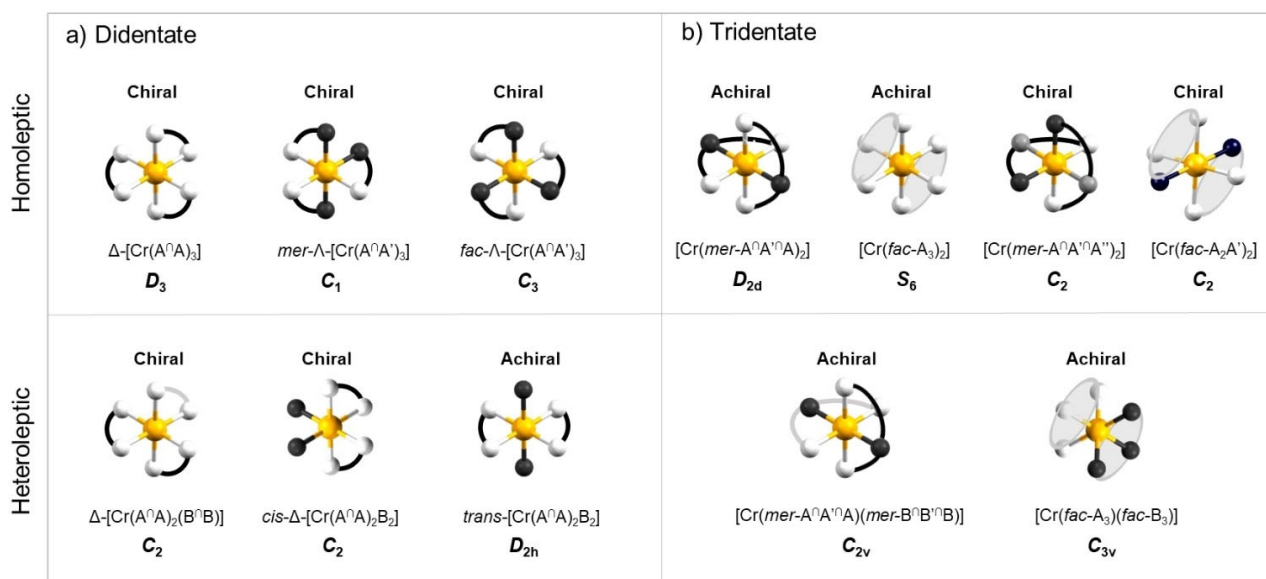European Chemical
Societies Publishing

Figure 1. Schematic representation of selected homoleptic and heteroleptic six-coordinate Cr(III) complexes with a) didentate and b) tridentate chelate ligands.

(pyrid-2-yl)ethane) belongs to the S_6-symmetrical point group ([Cr(fac-A$_3$)$_2$] in Figure 1b top).[25] The situation does not significantly change for the heteroleptic C_{2v}-symmetrical [Cr-(mer-A∩A'∩A)(mer-B∩B'∩B)] and C_{3v}-symmetrical [Cr(fac-A$_3$)(fac-B$_3$)] analogues (Figure 1b bottom). Chirality indeed emerges when unsymmetrical planar ligands are wrapped around the metal ion leading, for instance, to chiral C_2-symmetrical [Cr(mer-A∩A'∩A'')$_2$] and [Cr(fac-A$_2$A')$_2$] complexes (Figure 1b top). To the best of our knowledge no examples of the latter two chiral complexes have been reported for Cr(III). Finally, non-planar multidendate ligands can enable complexes gaining dissymmetry, as discussed in section 2.3.

2.2. Chirality Brought by Chiral Ligands

To circumvent non-chiral symmetries, the standard strategy consists in connecting inherent chiral ligands to the metal center. In this way, several stereogenic derivatives as the R/S-1,2-diaminopropane (R/S-pn) served for the synthesis of optically active complex such as [Cr(R/S-pn)(CN)$_4$] compounds,[26] derived from the C_{2v}-symmetrical achiral [Cr-(A∩A)B$_4$] building block. The central chirality of organic compounds was also combined with the complexes helical chirality (section 2.1 above) resulting in pairs of diastereomers, often with the added benefit of diastereoselective self-sorting and the use of conventional chromatography techniques for separation purpose. For instance, Benedetti *et al.* investigated chirality transfer in a series of tris-chelates Cr(III) complexes based on dithiophosphates.[27] Starting from enantiopure (+)-(S)(S)-Mebdtp, they evidenced the diastereoselective formation of the complex Λ-(−)-[Cr{(+)-(S)(S)-Mebdtp}$_3$] (Mebdtp=O, O'-bis(2-methylbutyl)dithiophosphato) in solution, while, surprisingly, the obtained crystallized compound displays

the opposite helical chirality Δ-(−)-[Cr{(+)-(S)(S)-Mebdtp}$_3$]. Diastereoisomeric crystallization was also early exploited with the connection of amino-acids to kinetically inert transition metals.[28]

2.3. Chirality Arising from Chelate Ring Conformation

The third strategy advancing over the past years in the design of chiral Cr(III) complexes, relies on flexible chelate ligands which are rigidified upon complexation. Flexible ligands can thus undergo a conformational twist upon complexation which removes symmetry axes of the second kind (Figure 2).

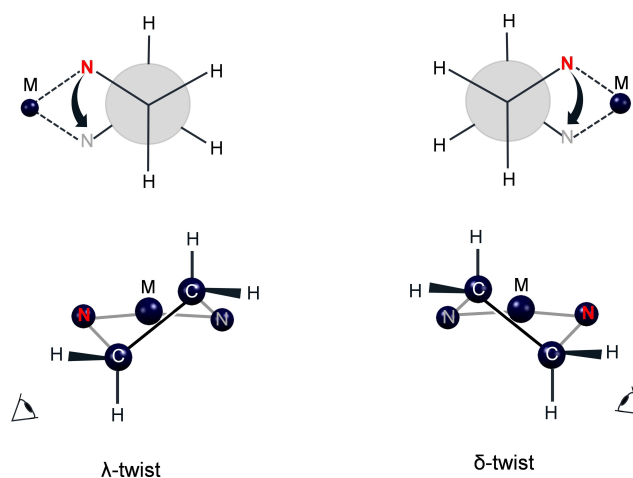This deviation from planarity within individual ring gives rise to inert δ/λ ligand conformations. A striking example of

Figure 2. Chiral conformational twists of a five-membered flexible didentate chelate ligand bound to a metal M.

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
European Chemical
Societies Publishing

this is given by the di(tridentate) ddpd (=N,N'-dimethyl-N,N'-dipyridine-2-yl-pyridine-2,6-diamine)[29] and dqp (=2,6-di-(quinolin-8-yl)pyridine)[16a] ligands in [Cr(ddpd)$_2$]$^{3+}$ and [Cr-(dqp)$_2$]$^{3+}$ complexes respectively, in which the chiral helical structures result from the ligand twist. Two kinds of stereo-descriptors can be assigned to these complexes: (i) P/M descriptors account for the whole structure configuration, where a right-hand helix is defined as P (plus) and the other way around for M (minus). (ii) δ/λ are associated to the stereochemistry of the individual chelate ring, δ for right-handed twisted ligands and λ for the opposite. Interestingly, for [Cr(ddpd)$_2$]$^{3+}$ and [Cr(dqp)$_2$]$^{3+}$, only the pairs of enantiomers PP/MM could be observed whereas the more constrained meso PM isomers are lacking.[30] Concerning didentate chelates, and despite ethylenediamine (en) being one of the most used ligand in the early Cr(III) coordination chemistry, the existence of these conformational twists was little referenced. Nevertheless, some reports on tris-ethylenediamine complexes suggested that the pair of diastereomers Λ-[M(δ-en)$_3$]$^{n+}$ and Δ-[M(λ-en)$_3$]$^{n+}$ (M=3d-block cations) is favored in the crystalline state.[31]

3. Circular Dichroism (CD) and Circularly Polarized Luminescence (CPL)

Among the chiroptical spectroscopies, circular dichroism (CD) is probably, the most used to extract qualitative and quantitative information (e.g. conformation, stability) from optically active materials. CD stems from the differential absorption of incident circularly polarized light by a chiral chromophore, i.e. its extinction coefficients for the right-circular (ε_R) and left-circular (ε_L) polarized beams are unequal at the considered wavelength. To depict the phenomenon, molar circular dichroism is plotted $\Delta\varepsilon = \varepsilon_R - \varepsilon_L$ as a function of the incident wavelength as shown in Figure 3a for the [Cr(dqp)$_2$]$^{3+}$ complex. When the sign of $\Delta\varepsilon$ changes, the effect is referred to as a Cotton Effect named after its discoverer.[32]

CD is temperature, solvent and concentration dependent and must be handled with care when comparing results.[33] Furthermore, if the two recorded spectra are mirror images, it does not necessarily mean that each sample is enantiopure, but only that the 'chiral content' is identical and opposite in each mixture. Therefore, prior to CD measurements, a quantitative chiral resolution is required if pure enantiomers are the target of the study. Their isolation is often demanding as enantiomers exhibit identical physico-chemical properties in a standard achiral medium and, must be configurationally stable. In that sense, the inertness of Cr(III) complexes was an added-value for their separation by cation-exchange chromatography using a chiral support,[34] capillary electrophoresis,[35] selective crystallisation using chiral counter ions,[36] chiral stationary phase HPLC[16b,30] as well as supercritical fluid chromatography.[37]

Contrary to the CD experiment where the sample is excited with a circularly polarized light source, in a CPL measurement,
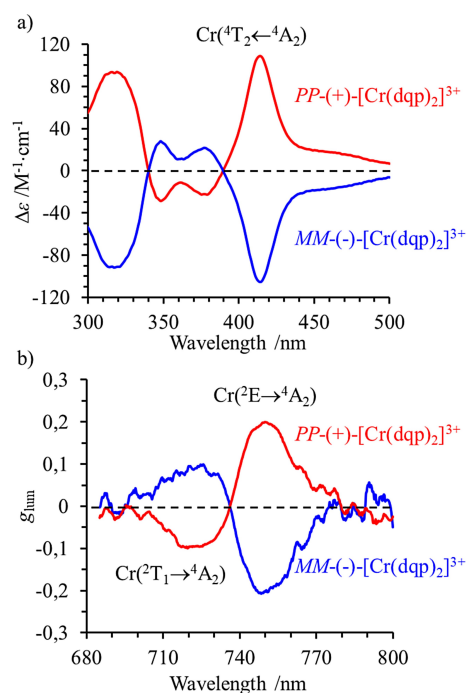

Figure 3. a) CD and b) CPL spectra of PP-(+)-[Cr(dqp)$_2$]$^{3+}$ and MM-(−)-[Cr(dqp)$_2$]$^{3+}$ complexes in CH$_3$CN solution at room temperature.

the sample is irradiated with non-polarized light in an energy domain where the photons are absorbed by the sample. Spontaneous emission from one of the emissive states of the chiral enantiopure molecule will have an excess of either the right or the left circularly polarized light. Both emissions are recorded, and the difference in intensity is plotted as a function of the wavelengths, giving the CPL spectrum (Figure 3b). To quantify this difference, the luminescence dissymmetry factor g_{lum} is introduced and defined in Equation (1) where I_L and I_R are the intensities of right and left circularly polarized emitted light, ΔI the difference in intensity and I the total intensity of emitted light.

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

When $g_{lum} = \pm 2$, the emission will consist only of RCP (Right Circularly Polarized) or LCP (Left Circularly Polarized) emitted light. Accordingly, $g_{lum} = 0$ corresponds to $I_L = I_R$ and unpolarised light emission. The luminescence dissymmetry factor can be rewritten using the rotatory strength R_{ij} normalised by the dipole strength D_{ij} (Equation 2 left). Both parameters can be related to the well-known electric $|\overrightarrow{\mu_{ij}}|$ and magnetic $|\overrightarrow{m_{ij}}|$ transition dipole moments together with the angle θ between them [Equation (2) centre].[6b,38]

$$g_{lum} = 4\frac{R_{ij}}{D_{ij}} = 4\frac{|\overrightarrow{\mu_{ij}}| \cdot |\overrightarrow{m_{ij}}| \cdot \cos\theta}{|\overrightarrow{\mu_{ij}}|^2 + |\overrightarrow{m_{ij}}|^2} = 4\frac{|\overrightarrow{\mu_{ij}}|/|\overrightarrow{m_{ij}}| \cdot \cos\theta}{(|\overrightarrow{\mu_{ij}}|/|\overrightarrow{m_{ij}}|)^2 + 1} \tag{2}$$

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
European Chemical
Societies Publishing

This equation can be rewritten for highlighting the ratio $r = |\vec{\mu_{ij}}|/|\vec{m_{ij}}|$ [Equation (2) right]. Consequently, g_{lum} reaches a maximum when (i) $r = 1$ ($|\vec{\mu_{ij}}| = |\vec{m_{ij}}|$) and (ii) the vectors are collinear ($\cos\theta = 1$).[39]

In most cases, the intense emission bands correspond to electric dipole allowed transitions with $|\vec{\mu_{ij}}| \gg |\vec{m_{ij}}|$ and g_{lum} is (desperately) weak as often found for organic chromophores. A cure requires electric dipole forbidden/magnetic dipole allowed transitions in order to get $|\vec{\mu_{ij}}|$ in the same range as $|\vec{m_{ij}}|$. The Laporte forbidden f-f intrashell transitions ($\Delta L = 0$) fit these criteria and are therefore valuable candidates for producing high dissymmetry factors. Because of the interest of using cheaper and earth-abundant d-block metals, the focus will be laid on 3d cores. However, pure metal-centered emissions along the 3d-block series is less common than in 4f elements because of vibrational coupling and ligand-metal orbitals mixing. Therefore, an electronic transition with an almost pure d-d character with a large enough energy gap is rare along the first transition series. Closed shell d^{10} cores (Zn(II) and Cu(I)) have been extensively used, but their dissymmetry factor remained small ($10^{-2} \leq g_{lum} \leq 10^{-4}$) as the emission involves ligand-centered levels.[40] Open shell cores were therefore studied and CPL activity were measured for d-d transitions in Mn(II)[41] and in Cr(III).[16] Due to its d^3 electronic configuration, pseudo-octahedral [CrL$_6$] chromophores display two magnetically-allowed but electric-dipole forbidden Cr($^2E \rightarrow ^4A_2$) and Cr($^2T_1 \rightarrow ^4A_2$) spin-flip transitions ($\Delta L = 0$, $\Delta S \neq 0$) which fulfil the conditions to maximise g_{lum} (Figure 4).

4. Chiroptical Properties of Chromium(III) Complexes

Early examples of tris-didentate chiral complexes, such as $(-)$-[Cr(en)$_3$]$^{3+}$ (chirality sections 2.1 & 2.3) were separated in the late 1960s and then characterized for their chiroptical properties ($g_{lum} = -0.046$ (14900 cm^{-1}); $\Delta\varepsilon_{max} = -1.44$ (21750 cm^{-1})).[2a]
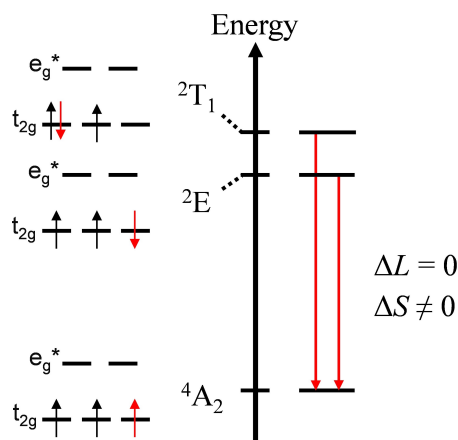

Figure 4. Energy level diagram for a [Cr(III)N]$_6$ ion in octahedral symmetry. The two spin-flip emissions are shown in red on the right and the electronic configuration of the states is highlighted on the left.

Kaizaki *et al.* then studied many homoleptic and heteroleptic compounds with helical chirality such as $(+)_{546}$-[Cr(pn)$_3$]$^{3+}$ ($\Delta\varepsilon_{max} = +0.34$ M^{-1}cm^{-1} (20900 cm^{-1}),) or $(-)_{589}$-[Cr(ox)(bpy)(phen)]$^{3+}$ ($\Delta\varepsilon_{max} = -1.76$ M^{-1}cm^{-1} (20500 cm^{-1})).[42] Maybe because of (i) a limited access to adapted instrumentation and (ii) some complexes were not emissive, only few CPL measurements have been reported whereas CD spectrum were systematically recorded (Table 1). Near the turn of the last century, CD and CPL responses of stereogenic ligands based-tris(chelate) Cr(III) complexes were studied in addition to their inherent helical geometry (see section 2.2) such as for Λ-fac-[Cr(L-ala)$_3$]$^{3+}$ complex ($g_{lum} = -0.021$ (14185 cm^{-1})).[43] This latter displays dissymmetry factors in the same range as those observed for $(-)$-[Cr(en)$_3$]$^{3+}$. More recently, chirality arising from chelate rings conformation (see section 2.3) started to be systematically exploited with Cr(III) cores in the field of CD and CPL. Although rigid and planar tridentate 5-membered ring chelates form only achiral complexes, flexible tridentate 6-membered ring chelates adopt helical conformation upon complexation to Cr(III) to give [Cr(ddpd)$_2$]$^{3+}$ and [Cr(dqp)$_2$]$^{3+}$.[16] Subsequent separation on chiral phases provided pure *PP* and *MM* enantiomers, for which large dissymmetry factor could be obtained with a record of g_{lum} of 0.2 and 0.1 for the Cr($^2E \rightarrow ^4A_2$) and Cr($^2T_1 \rightarrow ^4A_2$) transitions in [Cr(dqp)$_2$]$^{3+}$.[16a] These values are the highest reported to date for a Cr(III) complex and are comparable to those reported for lanthanide-based chiral complexes. The observed properties make these Cr(III) complexes potential sensitizers for CPL applications such as CPL lasers or CP-OLEDs. Chiral Cr(III) complexes for which a CD and/or a CPL spectra were recorded are compiled in Table 1.

Contrary to intrashell f$\rightarrow$f electronic transitions which have been thoroughly investigated for the mechanisms responsible for their CPL signatures in various chiral environments, similar studies are lacking for spin-flip intrashell d-d transitions occurring in Cr(III) complexes. In this context, only few reports can be found in the literature, among which the structural similarities between [Cr(ddpd)$_2$]$^{3+}$ (Table 1, entry 47) and [Cr(dqp)$_2$]$^{3+}$ (Table 1, entry 48) complexes are difficult to correlate with their strikingly different dissymmetry factors of $g_{lum} = 0.093$ and 0.2, respectively. One realizes that minor changes in the coordination sphere of a chiral Cr(III) complex can drastically alter the value of the dissymmetry factor without structural/electronic rationalization reported at the time of this mini-review. On the other hand, moving from isolated molecules to supramolecular materials is known to increase g_{lum} because of the better match between the excitation wavelength and the size of the optically active edifice.[8] Chromium complexes seem to follow this trend since Δ-$(-)$-[Cr(en)$_3$]$^{3+}$ doped in [Rh(en)$_3$Cl$_3$]·NaCl·6H$_2$O possesses $g_{lum} = -0.19$ ($\nu_{exc} = 14900$ cm^{-1})[58] whereas molecular and isolated Δ-$(-)$-[Cr(en)$_3$]$^{3+}$ shows only $g_{lum} = 0.046$ at the excitation energy.[46] Finally, the most comprehensive model used for rationalizing the influence of stereogenic centers on the optical activity (CD or CPL) is referred to as the independent systems/perturbation model (ISP).[66] According to this approach, the rotatory strength emerges from two distinct mechanisms: the static coupling (SC) and the dynamic coupling (DC). Applied to chiral

© 2021 The Authors. ChemPhotoChem published by Wiley-VCH GmbH

These are not the final page numbers! ↗↗

Table 1. CD or CPL characteristics reported for chiral six-coordinate pseudo-octahedral Cr(III) complexes at room temperature.

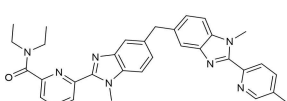| Entry	Complex	Chirality[a]	CD: $\Delta\varepsilon$ [M^{-1}cm^{-1}]	CPL: g_{lum} φ[%], τ[ms]	X-ray structure	Ref.
1	[Cr(CN)$_4$(d-pn)] pn = 1,2-propylendiamine	2.2	+0.075 (22660 cm^{-1}) −0.384 (25540 cm^{-1}) +0.052 (32260 cm^{-1})	No	No	[26]
2	[Cr(CN)$_4$(l-pn)] pn = 1,2-propylendiamine	2.2	−0.081 (22620 cm^{-1}) +0.383 (25410 cm^{-1}) −0.059 (30170 cm^{-1})	No	No	[26]
3	Λ-cis-(−)$_{598}$-[Cr(CN)$_2$(d-pn)$_2$] pn = 1,2-propylendiamine	2.1, 2.2	+0.484 (21810 cm^{-1}) −0.196 (24210 cm^{-1}) +0.040 (28410 cm^{-1})	No	Yes[44]	[26,44]
4	cis-(−)$_{598}$-[Cr(CN)$_2$(l-pn)$_2$] pn = 1,2-propylendiamine	2.1, 2.2	−0.557 (21880 cm^{-1}) +0.219 (24240 cm^{-1}) −0.059 (28330 cm^{-1})	No	No	[26]
5	cis-(+)$_{598}$-[Cr(CN)$_2$(d-pn)(l-pn)] pn = 1,2-propylendiamine	2.1, 2.2	+0.580 (23530 cm^{-1}) −0.045 (29590 cm^{-1})	No	No	[26]
6	cis-(−)$_{598}$-[Cr(CN)$_2$(d-pn)(l-pn)] pn = 1,2-propylendiamine	2.1, 2.2	−0.573 (23530 cm^{-1}) +0.050 (29590 cm^{-1})	No	No	[26]
7	cis-(+)$_{598}$-[Cr(CN)$_2$(en)$_2$]	2.1, 2.3	+0.00065 (14510 cm^{-1}) −0.00072 (14750 cm^{-1}) +0.51 (23330 cm^{-1}) −0.036 (29850 cm^{-1})	No	No	[26,45]
8	(−)$_{546}$-[Cr(en)$_3$] en = ethylenediamine	2.1, 2.3	−0.016 (14950 cm^{-1}) +0.007 (15250 cm^{-1}) −0.007 (15550 cm^{-1}) −1.44 (21750 cm^{-1})[46]	−0.046 (14900 cm^{-1})[46]	No	[46–47]
9	(+)$_{546}$-[Cr(en)$_3$]	2.1, 2.3	+0.0089 (15000 cm^{-1}) −0.0057 (15500 cm^{-1}) +0.0068 (15800 cm^{-1}) +1.49 (21900 cm^{-1})[42]	+0.028 (14880 cm^{-1})[2a] [b] φ = 0.0065%	Yes[47]	[2a,42, 47]
10	(+)$_{546}$-[Cr(phen)$_3$] phen = phenanthroline	2.1	+0.0128 (13800 cm^{-1}) −0.0077 (14500 cm^{-1}) +2.48 (21900 cm^{-1})	No τ = 0.224 ms	Yes[48]	[42,48]

These are not the final page numbers! ↗↗

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
European Chemical
Societies Publishing

Table 1. continued					
Entry	Complex	Chirality[a]	CD: $\Delta\varepsilon$ [M^{-1} cm^{-1}]	CPL: g_{lum} ϕ[%], τ[ms]	X-ray structure	Ref.
11	Δ-[Cr(bpy)$_3$] bpy = 2,2'-bipyridine	2.1	−1.2 (21739 cm^{-1}) −19.5 (28090 cm^{-1}) −21 (28818 cm^{-1}) −75 (31746 cm^{-1}) 9.5 (34898 cm^{-1}) 9 (35714 cm^{-1}) 12 (37879 cm^{-1})[49]	No	Yes[50]	[49–50]
12	Λ-[Cr(ox)$_3$] ox = oxalate	2.1	Yes	No	Yes[51]	[51–52]
13	Λ-[Cr(mal)$_3$] Mal = malonate	2.1	Yes	No	No	[52]
14	Λ-[Cr(thiox)$_3$] Thiox = dithioxalate	2.1	Yes	No	No	[52]
15	[Cr(Oacac)$_3$] Oacac = 3-octylpentane-2,4-dionato	2.1	$g = \Delta\varepsilon/\varepsilon =$ −0.04 (18868 cm^{-1}) +0.025 (15798 cm^{-1})[53] −10 (11765 cm^{-1}) −50 (~28570 cm^{-1}) [37]	No	No	[37,53]
16	[Cr(3-Buacac)$_3$] Buacac = 3-butylpentane-2,4-dionato	2.1	$g = \Delta\varepsilon/\varepsilon =$ −0.05 (19048 cm^{-1}) 0.032 (15798 cm^{-1})[54] −40 (~28570 cm^{-1}) [37]	No	No	[37,54]
17	[Cr(Pracac)$_3$] Pracac = 3-Propylpentane-2,4-dionato	2.1	$g = \Delta\varepsilon/\varepsilon =$ −0.05 (19048 cm^{-1}) +0.032 (15798 cm^{-1})	No	No	[55]
18	[Cr(Peacac)$_3$] Peacac = 3-Pentylpentane-2,4-dionato	2.1	$g = \Delta\varepsilon/\varepsilon =$ −0.05 (19048 cm^{-1}) +0.032 (15798 cm^{-1})	No	No	[55]
19	[Cr(en)$_3$][Cr(ox)$_3$] double salt	2.1, 2.3	Yes	+0.008 (14131 cm^{-1})	Yes[56]	[56–57]
20	[Cr(pn)$_3$][Cr(ox)$_3$] double salt pn = 1,3 propylendiamine	2.1, 2.3	Yes	No	Yes	[57]
21	(+)$_{546}$-[Cr(pn)$_3$] pn = 1,3 propylendiamine	2.1, 2.3	+0.0022 (15100 cm^{-1}) −0.0005 (15600 cm^{-1}) +0.0011 (15900 cm^{-1}) +0.34 (20900 cm^{-1})	No	No	[42]
22	(+)$_{546}$-[Cr(ox)$_2$(en)]	2.1, 2.3	+0.0075 (14500 cm^{-1}) −0.00103 (14900 cm^{-1}) +0.00113 (15300 cm^{-1}) −0.05 (16800 cm^{-1}) +2.00 (19400 cm^{-1})	No	Yes[56]	[42,56]
23	(+)$_{589}$-[Cr(ox)$_2$(bpy)]	2.1	+0.0045 (13900 cm^{-1}) −0.0054 (14300 cm^{-1}) −0.0066 (14500 cm^{-1}) +0.0017 (14800 cm^{-1}) −0.12 (17000 cm^{-1})	No	No	[42]

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

**Chemistry
Europe**

European Chemical
Societies Publishing

	Table 1. continued					
Entry	Complex	Chirality[a]	CD: $\Delta\varepsilon$ [M^{-1}cm^{-1}]	CPL: g_{lum} ϕ[%], τ[ms]	X-ray structure	Ref.
			+2.22 (19500 cm^{-1})			
24	(+)$_{546}$-[Cr(ox)$_2$(phen)]	2.1	+0.032 (13900 cm^{-1}) −0.0030 (14400 cm^{-1}) +0.027 (14700 cm^{-1}) −0.135 (16400 cm^{-1}) +2.46 (19000 cm^{-1})	No	No	[42]
25	(+)$_{546}$-[Cr(ox)(en)$_2$]	2.1, 2.3	+0.0129 (14700 cm^{-1}) −0.0064 (15200 cm^{-1}) +0.0114 (15500 cm^{-1}) +1.97 (20800 cm^{-1})	No	No	[42]
26	(+)$_{546}$-[Cr(ox)(bpy)$_2$]	2.1	+0.0056 (13600 cm^{-1}) −0.0017 (14000 cm^{-1}) −0.0030 (14300 cm^{-1}) +0.0020 (14900 cm^{-1}) −0.06 (17800 cm^{-1}) +1.40 (20600 cm^{-1})	No	No	[42]
27	(+)$_{589}$-[Cr(ox)(phen)$_2$]	2.1	+0.0046 (13800 cm^{-1}) −0.0062 (14800 cm^{-1}) −0.84 (18400 cm^{-1}) +1.50 (21200 cm^{-1})	No	No	[42]
28	(−)$_{589}$- [Cr(ox)(bpy)(phen)]	2.1	−0.0052 (13600 cm^{-1}) +0.0021 (14300 cm^{-1}) −1.76 (20500 cm^{-1})	No	No	[42]
29	(−)$_{589}$-[Cr(biguanide)$_3$]	2.1	−0.008 (13100 cm^{-1}) +0.004 (14100 cm^{-1}) −2.78 (19200 cm^{-1}) +4.16 (21700 cm^{-1})	No	No	[42]
30	(+)$_{546}$-[Cr(acac)(en)$_2$] acac = acetylacetonate	2.1, 2.3	+0.010 (13800 cm^{-1}) −0.0013 (14200 cm^{-1}) +0.077 (15200 cm^{-1}) +2.75 (21100 cm^{-1})	No	No	[42]
31	(+)$_{546}$-[Cr(acaCl)(en)$_2$] acaCl = 3-chloroacetylacetonato	2.1, 2.3	+0.0078 (13700 cm^{-1}) −0.0032 (14200 cm^{-1}) +0.069 (15100 cm^{-1}) +2.62 (21100 cm^{-1})	No	No	[42]
32	(+)$_{546}$-[Cr(acaBr)(en)$_2$ acaBr = 3-bromoacetylacetonato	2.1, 2.3	+0.0054 (13700 cm^{-1}) −0.0056 (14200 cm^{-1})	No	No	[42]

These are not the final page numbers! ↗↗

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
European Chemical
Societies Publishing

Table 1.	continued					
Entry	Complex	Chirality[a]	CD: $\Delta\varepsilon$ [M^{-1}cm^{-1}]	CPL: g_{lum} ϕ[%], τ[ms]	X-ray structure	Ref.
			+0.048 (15200 cm^{-1}) +2.38 (21200 cm^{-1})			
33	(+)$_{546}$-[Cr(acac)$_2$(en)]	2.1, 2.3	−0.0119 (12900 cm^{-1}) +0.056 (13900 cm^{-1}) −0.0224 (14400 cm^{-1}) −0.84 (17700 cm^{-1}) +4.00 (20100 cm^{-1})	No	No	[42]
34	(+)$_{546}$-[Cr(acac)(acaBr)(en)]	2.1, 2.3	−0.0139 (12700 cm^{-1}) +0.0483 (13800 cm^{-1}) −0.0543 (14400 cm^{-1}) −0.84 (17700 cm^{-1}) +3.59 (20100 cm^{-1})	No	No	[42]
35	(+)$_{546}$-[Cr(acaBr)$_2$(en)]	2.1, 2.3	−0.88 (17300 cm^{-1}) +4.40 (20200 cm^{-1})	No	No	[42]
36	(+)$_{546}$-[Cr(acaCl)$_2$(en)]	2.1, 2.3	−0.0252 (12600 cm^{-1}) +0.0545 (13700 cm^{-1}) −0.0603 (14500 cm^{-1}) −0.86 (17700 cm^{-1}) +4.21 (20200 cm^{-1})	No	No	[42]
37	Δ-(−)-[Cr(en)$_3$]$^{3+}$ doped in 2[Rh(en)$_3$Cl$_3$]·NaCl·6H$_2$O	2.1, 2.3	Yes	−0.19 (14900 cm^{-1})	Yes	[58]
38	(+)$_{589}$-[Cr(gly)(en)$_2$] gly = glycine	2.1, 2.3	+0.00777 (14810 cm^{-1}) −0.00158 (15150 cm^{-1}) +0.00604 (15580 cm^{-1}) +1.91 (21460 cm^{-1}) −0.16 (27550 cm^{-1}) +0.04 (30450 cm^{-1})	No	No	[59]
39	(+)$_{589}$-[Cr(L-ala)(en)$_2$] ala = alanine	2.1, 2.2, 2.3	+0.00664 (14770 cm^{-1}) −0.00125 (15280 cm^{-1}) +0.00270 (15570 cm^{-1}) +1.65 (21150 cm^{-1}) −0.12 (27700 cm^{-1}) +0.04 (30400 cm^{-1})	No	No	[59]
40	(+)$_{589}$-[Cr(phala)(en)$_2$] phala = phenylalanine	2.1, 2.2, 2.3	+0.00725 (14750 cm^{-1}) −0.00118 (15200 cm^{-1}) +0.00385 (15520 cm^{-1}) +1.70 (21100 cm^{-1}) −0.16 (27620 cm^{-1}) +0.03 (30530 cm^{-1})	No	No	[59]
41	Λ-fac-[Cr(L-ala)$_3$]	2.1, 2.2	Yes	−0.021 (14185 cm^{-1})[c]	No	[43]
42	[Cr(D-ala)$_3$]	2.1, 2.2	Yes	+0.024 (14185 cm^{-1})[c]	No	[43]
43	(+)$_{598}$-[Cr(d-pn)$_3$] pn = 1,2-propylendiamine	2.1, 2.2	+1.805 (21230 cm^{-1}) −0.040 (24390 cm^{-1})	No	No	[26]

These are not the final page numbers! ↗↗

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
European Chemical
Societies Publishing

Table 1. continued					
Entry	Complex	Chirality[a]	CD: $\Delta\varepsilon$ [M^{-1}cm^{-1}]	CPL: g_{lum} ϕ[%], τ[ms]	X-ray structure	Ref.
			$+0.095$ (27400 cm^{-1}) $+0.103$ (29670 cm^{-1})			
44	$(-)_{598}$-[Cr(l-pn)$_3$] pn = 1,2-propylendiamine	2.1, 2.2	-1.792 (21230 cm^{-1}) $+0.041$ (24390 cm^{-1}) -0.098 (27250 cm^{-1}) -0.112 (29410 cm^{-1})	No	No	[26]
45	Δ-$(+)_{589}$-[Cr{(-)(R,R)bdtp}$_3$] bdtp = cyclo- O,O'1(R), 2(R)-dimethyl-ethylene dithio-phosphato	2.1, 2.2	Yes	No	Yes	[60]
46	Λ-$(-)$-[Cr{(+)-(S)(S)-Mebdtp}$_3$] Mebdtp = O, O'-[bis(2-methylbutyl)]dithiophosphato	2.1, 2.2	Yes	No	No	[27]
47	(M,M)-[Cr(ddpd)$_2$] ddpd = N,N'-dimethyl-N,N'-dipyridine-2-yl-pyridine-2,6-diamine	2.3	Yes Maximum at 300 nm	-0.093 (12900 cm^{-1}) $\phi = 11\%$; $\tau = 0.889$ ms	Yes	[16b,29]
48	(P,P)-$(+)$-[Cr(dqp)$_2$] dqp = 2,6-di(quinolin-8-yl)pyridine	2.3	~90 (31447 cm^{-1}) ~110 (24155 cm^{-1})	$+0.2$ (13351 cm^{-1}) -0.1 (13736 cm^{-1}) $\phi = 5.1\%$; $\tau = 1.2$ ms	Yes	[16a]
49	(P,P)-[Cr(dqpOMe)$_2$] dqpOMe = 4-methoxy-2,6-di(quinolin-8-yl)pyridine	2.3	~90 (~30300 cm^{-1}) ~100 (~25000 cm^{-1})	$+0.18$ (13228 cm^{-1}) -0.08 (13831 cm^{-1}) $\phi = 17\%$; $\tau = 1.35$ ms	Yes	[30]
50	(P,P)-[Cr(dqpBr)$_2$] dqpBr = 4-bromo-2,6-di(quinolin-8-yl)pyridine	2.3	~90 (~30300 cm^{-1}) ~100 (~24400 cm^{-1})	$+0.19$ (13316 cm^{-1}) -0.07 (13870 cm^{-1}) $\phi = 14\%$; $\tau = 1.23$ ms	Yes	[30]
51	(P,P)-[Cr(dqpC≡CH)$_2$] dqpC≡CH = 4-Alkyne-2,6-di(quinolin-8-yl)pyridine	2.3	~110 (~30300 cm^{-1}) ~100 (~24400 cm^{-1})	$+0.17$ (13280 cm^{-1}) -0.06 (13850 cm^{-1}) $\phi = 15\%$; $\tau = 1.33$ ms	Yes	[30]
52	Λ-$(-)_{598}$-$trans$-(O$_5$O$_6$)-[Cr(eda3p)] eda3p = ethylenediamine-N-acetato-N,N',N'-tri-3-propionate	2.3	$+0.09$ (16580 cm^{-1}) -0.64 (18760 cm^{-1}) -0.14 (21050 cm^{-1}) $+0.07$ (23530 cm^{-1}) $+0.23$ (26670 cm^{-1})	No	No	[61]
53	Λ-$(-)_{598}$-$trans$-(O$_5$)-[Cr(eddda)] Eddda = Ethylenediamine-N,N'-diacetato-N,N'-dipropionate	2.3	$+0.0352$ (14250 cm^{-1}) -0.0092 (14870 cm^{-1}) $+0.0780$ (15260 cm^{-1}) $+0.207$ (16530 cm^{-1}) -0.765 (18620 cm^{-1}) -0.19 (20330 cm^{-1}) -0.05 (22170 cm^{-1}) -0.075 (24100 cm^{-1}) $+0.23$ (26530 cm^{-1})	No	No	[62]
54	Λ-$(+)_{598}$-$trans$-(O$_5$)-[Cr(S,S-edds)] S,S-edds = (S,S)-2,2'-(ethylenediimino) disuccinate	2.2, 2.3	$+0.0348$ (14210 cm^{-1}) -0.0024 (14380 cm^{-1}) $+0.0036$ (14530 cm^{-1}) -0.0120 (14870 cm^{-1}) $+0.0690$ (15440 cm^{-1}) $+0.409$ (17540 cm^{-1}) -0.396 (19330 cm^{-1})	No	No	[62]

Table 1. continued						
Entry	Complex	Chirality[a]	CD: $\Delta\varepsilon$ [M^{-1} cm^{-1}]	CPL: g_{lum} ϕ[%], τ[ms]	X-ray structure	Ref.
			+0.453 (21830 cm^{-1}) +0.33 (23330 cm^{-1}) +0.386 (27030 cm^{-1})			
55	Λ-(+)$_{598}$-[Cr(S,S-ptnta)] S,S-ptnta = (2S,4S)-2,4-pentanediamine tetraacetate	2.2, 2.3	−0.0038 (13920 cm^{-1}) +0.0055 (14350 cm^{-1}) +0.0058 (14460 cm^{-1}) −0.0017 (14620 cm^{-1}) +0.0014 (14620 cm^{-1}) −0.0021 (15000 cm^{-1}) +0.0260 (15310 cm^{-1}) +0.2 (18000 cm^{-1}) +0.442 (19670 cm^{-1}) −0.064 (21670 cm^{-1}) +0.435 (24000 cm^{-1}) +0.27 (25250 cm^{-1}) −0.024 (29660 cm^{-1})	No	No	[62a]
56	(−)$_{589}$-[Cr$_2$(OH)$_2$(bpy)$_2$(phen)$_2$]	2.1	−0.0766 (13700 cm^{-1}) −0.0920 (14100 cm^{-1}) +0.0083 (15500 cm^{-1}) −6.82 (18700 cm^{-1})	No	No	[42]
57	[Cr$_2$(l-tart$_2$H)(bpy)$_2$] l-tart = L-tartrate	2.1, 2.2	Yes	No	No	[63]
58	[Cr$_2$(l-tart$_2$H)(phen)$_2$]	2.1, 2.2	Yes	No	Yes	[63–64]
59	[Cr$_2$(OH)$_2$(L-ala)$_4$]	2.1, 2.2	Yes	Yes[c]	No	[59]
60	M-(+)$_{589}$-[Cr(L)$_3$]$^{3+}$ L =	2.1	−22 (31750 cm^{-1}) +48 (29070 cm^{-1}) +1.8 (21500 cm^{-1})	No	No	[34]
61	(M,M)-(−)$_{589}$-[LnCr(L)$_3$]$^{6+}$ Ln = Eu, Gd, Tb	2.1	−74 (29410 cm^{-1})	+0.01 (13423 cm^{-1}) +0.07 (16234 cm^{-1}) (identical for all Ln)	Yes for Eu	[34]
62	(Λ)- and (Δ)-[(acac)$_2$Cr(ox)Ln(HBpz$_3$)$_2$] Ln = Yb, Dy, Sm, Ho, Er HBpz$_3^-$ = hydrotris(pyrazol-1-yl)borato	2.1	Yes	No	Yes for Yb, Sm, Ho and Er	[65]

[a] Type of chirality defined in sections 2.1, 2.2 and 2.3. [b] Measurement done in a solid at 195 K, [c] Measurement done at 77 K. The quantum yields (ϕ) and excited-state lifetimes (τ) were measured in deaerated solutions.

lanthanide complexes, the DC mechanism appears to be very efficient and may provide considerable rotatory strength and therefore large dissymmetry factor. It can be exemplified in Cs[Eu(hfbc)$_4$] (hfbc = heptafluorobutyrylcamphorate) complex, in which an essentially achiral square anti-prismatic coordination sphere (twist angle of −41.4°) results in a weak static-coupling (SC) contribution, whereas the location of a camphor unit on the bound ligand is responsible for the impressive

dissymmetry factor via the dynamic coupling (DC) mechanism. Within the context of chiral Cr(III) complexes, a related observation can be made when comparing the Δ-(−)-[Cr-(en)$_3$]$^{3+}$ complexes, which show intrinsic chirality of the CrN$_6$ coordination sphere due to D_3 local symmetry and a modest g_{lum} of −0.046 via SC mechanism (Table 1, entry 8), with [Cr(dqp)$_2$]$^{3+}$ (Table 1, entry 48) where the considerable g_{lum} = 0.2 arises from the helical arrangement of the ligands and not

These are not the final page numbers! ↗↗

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry Europe
European Chemical
Societies Publishing

from the metal environment, This highlights the efficiency of the DC mechanism compared to SC and led us to suggest that the ISP model can be used to partially rationalize g_{lum} values between different Cr(III) chiral complexes.

5. Conclusions and Perspectives

Since the beginning of modern coordination chemistry and of photophysics, Cr(III) complexes have played an essential role in the development of these two correlated domains. This is mainly due to their kinetic inertness against ligand substitution and their light emission arising from the metal centered Cr(^{2}E) and Cr(^{2}T$_1$) states. The field of CPL is dominated by chiral organic chromophores and chiral metal complexes based on 4d, 5d and 4f elements. Recent results have demonstrated that chiral Cr(III) complexes have also a great potential, because chromium is a earth-abundant metal and because the electronic nature of the radiative Cr(^{2}T$_1$) and Cr(^{2}E) transitions fit the conditions to enhance the dissymmetric factor g_{lum}. Up to now, the record value reported for a chiral Cr(III) of g_{lum} is about 0.2 which indicates that there is still a huge gap to reach the maximized values of ± 2. This promising result together with the few literature reports on chiral Cr(III) complexes indicate that efforts should be made on the preparation of these chiral complexes. It is worth mentioning that computational calculations are as well fairly underexplored. Insights on computational theory are fundamentally important and should facilitate the design of chiral Cr(III) complexes. As shown in Table 1, the so far reported chiral Cr(III) complexes are mainly restricted to discrete mononuclear complexes (entries 1–55). It would be of interest to study how chiral Cr(III) complexes behave in polynuclear structures (entries 56–59) or in more sophisticated assemblies where additional sources of chirality can be present (entries 60–62). Moreover, the kinetic inertness of Cr(III) complexes should allow their insertion into macromolecular matrices or platforms like polymers where other phenomenon like exciton-coupling or long-range chirality can enhance the chiroptical properties.

Conflict of Interest

The authors declare no conflict of interest.

[1] B. N. Samojlov, *J. Exp. Theor. Phys.* **1948**, *18*, 1030-10140. .

[2] a) C. A. Emeis, L. J. Oosterhoff, *Chem. Phys. Lett.* **1967**, *1*, 129–132; b) C. A. Emeis, L. J. Oosterhoff, *J. Phys. Chem.* **1971**, *54*, 4809–4819.

[3] a) L. E. MacKenzie, R. Pal, *Nat. Chem. Rev.* **2021**, *5*, 109–124; b) J. R. Brandt, F. Salerno, M. J. Fuchter, *Nat. Chem. Rev.* **2017**, *1*, 0045; c) D.-W. Zhang, M. Li, C.-F. Chen, *Chem. Soc. Rev.* **2020**, *49*, 1331–1343; d) F. Zinna, M. Pasini, F. Galeotti, C. Botta, L. Di Bari, U. Giovanella, *Adv. Funct. Mater.* **2017**, *27*, 1603719.

[4] a) K. Staszak, K. Wieszczycka, V. Marturano, B. Tylkowski, *Coord. Chem. Rev.* **2019**, *397*, 76–90; b) R. Carr, N. H. Evans, D. Parker, *Chem. Soc. Rev.* **2012**, *41*, 7673–7686; c) M. C. Heffern, L. M. Matosziuk, T. J. Meade, *Chem. Rev.* **2014**, *114*, 4496–4539.

[5] a) E. S. Gauthier, L. Abella, N. Hellou, B. Darquié, E. Caytan, T. Roinsel, N. Vanthuyne, L. Favereau, M. Srebro-Hooper, J. A. G. Williams, J. Autschbach, J. Crassous, *Angew. Chem. Int. Ed.* **2020**, *59*, 8394–8400; *Angew. Chem.* **2020**, *132*, 8472–8478; b) N. Saleh, C. Shen, J. Crassous, *Chem. Sci.* **2014**, *5*, 3680–3694; c) E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz, S. de la Moya, *Chem. Eur. J.* **2015**, *21*, 13488–13500; d) L. Arrico, L. Di Bari, F. Zinna, *Chem. Eur. J.* **2021**, *27*, 2920–2934; e) H. Tanaka, Y. Inoue, T. Mori, *ChemPhotoChem* **2018**, *2*, 386–402; f) T. Mori, *Circularly Polarized Luminescence of Isolated Small Organic Molecules*, Springer Singapore, **2020**.

[6] a) F. Zinna, L. Di Bari, *Chirality* **2015**, *27*, 1–13; b) B. Doistau, J.-R. Jiménez, C. Piguet, *Front. Chem.* **2020**, *8*; c) M. Hasegawa, S. Sakurai, M. A. Yamaguchi, D. Iwasawa, N. Yajima, S. Ogata, Y. Inazuka, A. Ishii, K. Suzuki, *Photochem. Photobiol. Sci.* **2020**, *19*, 1054–1062.

[7] a) G. Albano, G. Pescitelli, L. Di Bari, *Chem. Rev.* **2020**, *120*, 10145–10243; b) Y. Yang, K.-Z. Wang, D. Yan, *Chem. Commun.* **2017**, *53*, 7752–7755; c) J. Wade, J. R. Brandt, D. Reger, F. Zinna, K. Y. Amsharov, N. Jux, D. L. Andrews, M. J. Fuchter, *Angew. Chem. Int. Ed.* **2021**, *60*, 222–227; *Angew. Chem.* **2021**, *133*, 224–229; d) J. L. Han, P. F. Duan, X. G. Li, M. H. Liu, *J. Am. Chem. Soc.* **2017**, *139*, 9783–9786; e) J. Kumar, T. Nakashima, T. Kawai, *J. Phys. Chem. Lett.* **2015**, *6*, 3445–3452; f) T. Zhao, J. Han, P. Duan, M. Liu, *Acc. Chem. Res.* **2020**, *53*, 1279–1292.

[8] J. L. Greenfield, J. Wade, J. R. Brandt, X. Shi, T. J. Penfold, M. J. Fuchter, *Chem. Sci.* **2021**, *41*, 8589–8602.

[9] a) F. S. Richardson, *Chem. Rev.* **1979**, *79*, 17–42; b) F. S. Richardson, *Inorg. Chem.* **1980**, *19*, 2806–2812.

[10] J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki, G. Muller, *J. Am. Chem. Soc.* **2008**, *130*, 13814–13815.

[11] a) O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533; b) L. A. Büldt, O. S. Wenger, *Chem. Sci.* **2017**, *8*, 7359–7367; c) C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057–1070.

[12] a) O. S. Wenger, *Chem. Eur. J.* **2019**, *25*, 6043–6052; b) O. S. Wenger, *Nat. Chem.* **2020**, *12*, 323–324; c) B. C. Paulus, K. C. Nielsen, C. R. Tichnell, M. C. Carey, J. K. McCusker, *J. Am. Chem. Soc.* **2021**, *143*, 8086–8098.

[13] T. H. Maiman, *Nature* **1960**, *187*, 493–494.

[14] a) D. T. Richens, *Chem. Rev.* **2005**, *105*, 1961–2002; b) L. Helm, A. E. Merbach, *Chem. Rev.* **2005**, *105*, 1923–1959.

[15] M. Cantuel, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, G. Hopfgartner, C. Piguet, *J. Chem. Soc. Dalton Trans.* **2002**, *9*, 1929–1940.

[16] a) J.-R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244–13252; b) C. Dee, F. Zinna, W. R. Kitzmann, G. Pescitelli, K. Heinze, L. Di Bari, M. Seitz, *Chem. Commun.* **2019**, *55*, 13078–13081.

[17] J.-A. Le Bel, *Bull. Soc. Chim. Fr.* **1874**, *22*, 337–347.

[18] J. H. Van't Hoff, *Arch. Neerl. Sci. Exactes Nat.* **1874**, *9*, 445–454.

[19] A. Werner, *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 121–130.

[20] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem. Int. Ed.* **1966**, *5*, 385–415; *Angew. Chem.* **1966**, *78*, 413–447.

[21] a) V. I. Sokolov, *Chirality and Optical Activity in Organometallic Compounds*, Gordon & Breach Sciences Publishers, New York, **1990**; b) M. G. H. Amouri, *Chirality in Transition Metals Chemistry: Molecules, Supramolecular Assemblies and Materials.*, Wiley-VCH, **2009**.

[22] J. Gal, *Chirality* **2011**, *23*, 1–16.

[23] a) C. J. Hawkins, *Absolute configuration of metal complexes*, Wiley-Interscience, New York, **1971**; b) A. V. Zelewsky, *Stereochemistry* **1996**.

[24] E. C. Constable, C. E. Housecroft, M. Neuburger, J. Schönle, J. A. Zampese, *Dalton Trans.* **2014**, *43*, 7227–7235.

[25] S. Treiling, C. F. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, *58*, 18075–18085; *Angew. Chem.* **2019**, *131*, 18243–18253.

[26] Y. Sakabe, H. Ogura, *Inorg. Chim. Acta* **1991**, *189*, 225–228.

[27] P. Biscarini, M. Benedetti, R. Kuroda, F. Ferranti, *Eur. J. Inorg. Chem.* **2006**, *2006*, 3167–3176.

ChemPhotoChem

Minireviews
doi.org/10.1002/cptc.202100146

Chemistry
Europe
European Chemical
Societies Publishing

[28] R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, C. F. Weick, *J. Chem. Soc. Dalton Trans.* **1974**, *13*, 1385–1396.

[29] S. Otto, M. Grabolle, C. Förtser, C. Kreitner, U. Resh-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572–11576; *Angew. Chem.* **2015**, *127*, 11735–11739.

[30] J.-R. Jiménez, M. Poncet, S. Míguez-Lago, S. Grass, J. Lacour, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *Angew. Chem. Int. Ed.* **2021**, *60*.

[31] E. C. Constable, C. E. Housecroft, *Chemistry* **2020**, *2*, 759–776.

[32] A. Cotton, *J. Phys. Theor. Appl.* **1896**, *5*, 290–302.

[33] a) Y. Nagata, T. Nishikawa, M. Suginome, *Chem. Commun.* **2012**, *48*, 11193–11195; b) K. Noack, A. J. Thomson, *Helv. Chim. Acta* **1981**, *64*, 2383–2392.

[34] M. Cantuel, G. Bernardinelli, G. Muller, J. P. Riehl, C. Piguet, *Inorg. Chem.* **2004**, *43*, 1840–1849.

[35] J. E. Harris, N. Desai, K. E. Seaver, R. T. Watson, N. A. P. Kane-Maguire, J. F. Wheeler, *J. Chromatogr. A* **2001**, *919*, 427–436.

[36] S. Sharma, F. Lombeck, L. Eriksson, O. Johansson, *Chem. Eur. J.* **2010**, *16*, 7078–7081.

[37] M. Cortijo, C. Viala, T. Reynaldo, L. Favereau, I. Fabing, M. Srebro-Hooper, N. Ratel-Ramond, J. Crassous, J. Bonvoisin, *Inorg. Chem.* **2017**, *56*, 4555–4567.

[38] a) J. P. Riehl, F. S. Richardson, *Chem. Rev.* **1986**, *86*, 1–16; b) J. Autschbach, *Chirality* **2009**, *21*, E116-E152.

[39] S. Wada, Y. Kitagawa, T. Nakanishi, M. Gon, K. Tanaka, K. Fushimi, Y. Chujo, Y. Hasegawa, *Sci. Rep.* **2018**, *8*, 16395.

[40] a) R. Aoki, R. Toyoda, J. F. Kögel, R. Sakamoto, J. Kumar, Y. Kitagawa, K. Harano, T. Kawai, H. Nishihara, *J. Am. Chem. Soc.* **2017**, *139*, 16024–16027; b) M. Deng, N. F. M. Mukthar, N. D. Schley, G. Ung, *Angew. Chem. Int. Ed.* **2020**, *59*, 1228–1231; *Angew. Chem.* **2020**, *132*, 1244–1247; c) J. F. Kögel, S. Kusaka, R. Sakamoto, T. Iwashima, M. Tsuchiya, R. Toyoda, R. Matsuoka, T. Tsukamoto, J. Yuasa, Y. Kitagawa, T. Kawai, H. Nishihara, *Angew. Chem. Int. Ed.* **2016**, *55*, 1377–1381; *Angew. Chem.* **2016**, *128*, 1399–1403.

[41] J. Zhao, T. Zhang, X.-Y. Dong, M.-E. Sun, C. Zhang, X. Li, Y. S. Zhao, S.-Q. Zang, *J. Am. Chem. Soc.* **2019**, *141*, 15755–15760.

[42] S. Kaizaki, J. Hidaka, Y. Shimura, *Inorg. Chem.* **1973**, *12*, 142–150.

[43] T. Tsubomura, I. Ohkouchi, M. Morita, *B. Chem. Soc. Jpn.* **1991**, *64*, 2341–2348.

[44] Y. Sakabe, H. Sakaguchi, H. Takayanagi, H. Ogura, Y. Iitaka, *Inorg. Chim. Acta* **1991**, *183*, 97–105.

[45] S. Kaizaki, J. Hidaka, Y. Shimura, *B. Chem. Soc. Jpn.* **1975**, *48*, 902–905.

[46] G. L. Hilmes, H. G. Brittain, F. S. Richardson, *Inorg. Chem.* **1977**, *16*, 528–533.

[47] A. Whuler, C. Brouty, P. Spinat, P. Herpin, *Acta Crystallogr. Sect. B* **1977**, *33*, 2877–2885.

[48] B. Doistau, G. Collet, E. Acuna Bolomey, V. Sadat-Noorbakhsh, C. Besnard, C. Piguet, *Inorg. Chem.* **2018**, *57*, 14362–14373.

[49] S. J. Milder, J. S. Gold, D. S. Kliger, *Inorg. Chem.* **1990**, *29*, 2506–2511.

[50] A. Hauser, M. Mäder, W. T. Robinson, R. Murugesan, J. Ferguson, *Inorg. Chem.* **1987**, *26*, 1331–1338.

[51] J. N. van Niekerk, F. R. L. Schoening, *Acta Crystallogr.* **1952**, *5*, 196–202.

[52] J. Fan, M. Seth, J. Autschbach, T. Ziegler, *Inorg. Chem.* **2008**, *47*, 11656–11668.

[53] N. Anzai, H. Kurihara, M. Sone, H. Furukawa, T. Watanabe, K. Horie, S. Kumar, *Liq. Cryst.* **2006**, *33*, 671–679.

[54] N. Anzai, S. Machida, K. Horie, *Chem. Lett.* **2001**, *30*, 888–889.

[55] N. Anzai, S. Machida, K. Horie, *Liq. Cryst.* **2003**, *30*, 359–366.

[56] X. Hua, K. Larsson, T. J. Neal, G. R. A. Wyllie, M. Shang, A. Graham Lappin, *Inorg. Chem. Commun.* **2001**, *4*, 635–639.

[57] M. Herren, H. Horikoshi, M. Morita, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1996**, *285*, 573–578.

[58] R. D. Peacock, B. Stewart, *J. Chem. Soc. Chem. Commun.* **1982**, *5*, 295–296.

[59] S. Kaizaki, M. Ito, *B. Chem. Soc. Jpn.* **1981**, *54*, 2499–2502.

[60] M. Benedetti, P. Biscarini, A. Brillante, E. Castrglioni, *Enantiomer* **1999**, *4*, 63–66.

[61] D. J. Radanović, M. I. Djuran, M. B. Dimitrijević, B. E. Douglas, *Inorg. Chim. Acta* **1991**, *186*, 13–19.

[62] a) S. Kaizaki, H. Mori, *B. Chem. Soc. Jpn.* **1981**, *54*, 3562–3565; b) D. J. Radanovic, B. E. Douglas, *J. Coord. Chem.* **1975**, *4*, 191–198.

[63] S. Kaizaki, J. Hidaka, Y. Shimura, *B. Chem. Soc. Jpn.* **1969**, *42*, 988–994.

[64] N. Koine, M. Iida, T. Sakai, N. Sakagami, S. Kaizaki, *J. Chem. Soc. Chem. Commun.* **1992**, *23*, 1714–1716.

[65] a) M. A. Subhan, T. Suzuki, S. Kaizaki, *J. Chem. Soc. Dalton Trans.* **2001**, 492–497; b) M. A. Subhan, T. Suzuki, S. Kaizaki, *J. Chem. Soc. Dalton Trans.* **2002**, *7*, 1416–1422.

[66] a) S. F. Mason, *J. Chem. Soc. A* **1971**, *0*, 667–676; b) S. F. Mason, R. H. Seal, *J. Chem. Soc. Chem. Commun.* **1975**, *9*, 331–333; c) S. F. Mason, R. H. Seal, *Mol. Phys.* **1976**, *31*, 755–775; d) F. S. Richardson, *J. Chem. Phys.* **1971**, *54*, 2453–2468; e) R. W. Strickland, F. S. Richardson, *J. Phys. Chem.* **1976**, *80*, 164–173.

MINIREVIEWS

Chromium wins the race? In the search for cheap circularly polarized luminescence probes with high quantum yields and high dissymmetry factors, chiral inert chromium(III) complexes are in the race due to recent drastic improvements. This minireview surveys the chiroptical properties of this class of compounds.
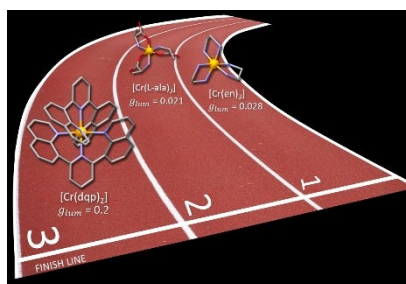
M. Poncet, Dr. A. Benchohra*, Dr. J.-R. Jiménez*, Prof. C. Piguet*

1 – 14

Chiral Chromium(III) Complexes as Promising Candidates for Circularly Polarized Luminescence

Special Collection