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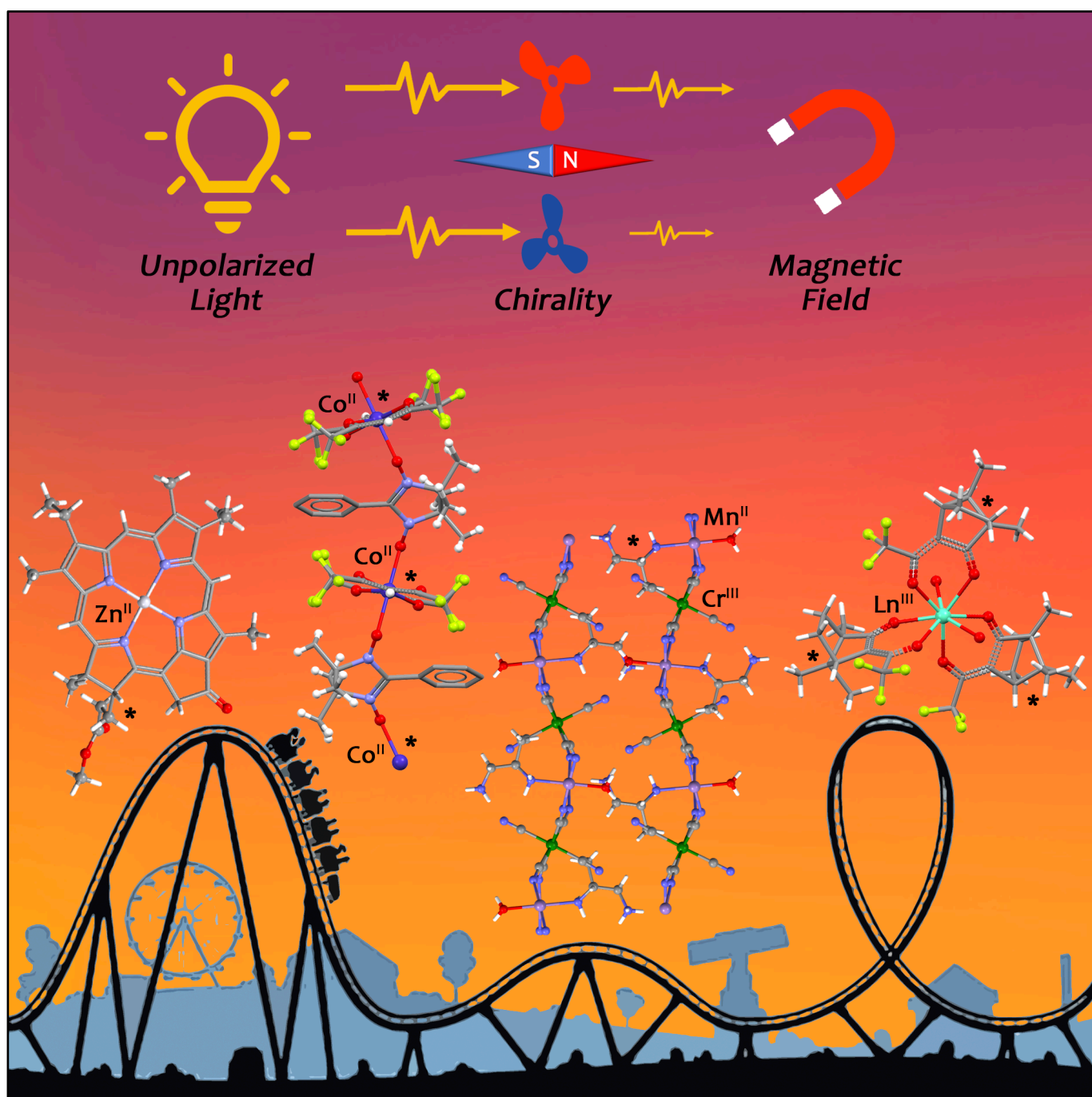
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Magneto-Chiral Dichroism: A Playground for Molecular Chemists

Matteo Atzori,^{*,[a]} Geert L. J. A. Rikken^[a] and Cyrille Train^[a]



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Abstract: Magneto-chiral dichroism (MChD) is a non-reciprocal manifestation of light-matter interaction that can be observed in chiral systems possessing a magnetization, either spontaneous or induced by an external magnetic field. It features a differential absorption or emission of unpolarized light that depends on the relative orientation of the magnetization with respect to the direction of light propagation and on the absolute configuration of the system. Molecular chemistry is the best-suited route towards systems combining chirality and magnetism. Nowadays, investigation of MChD is still in its infancy although this effect might play a fundamental role in technological applications, such as optical readout of magnetic data with unpolarized light. With this minireview, we aim at providing a precise description of this unconventional effect, recall the main results obtained so far and highlight the remaining challenges, underlining the opportunities opened to molecular chemists interested in investigating this fascinating effect with implications in chemistry and beyond.

1. Introduction

Interaction between chirality, light, and magnetism can afford fascinating manifestations of light-matter interaction. Investigations aimed at understanding their mutual relationship date back to the 19th century. In 1811 Arago discovered the natural optical activity (NOA) in chiral quartz crystals^[1] while in 1846 Faraday discovered the magnetically induced optical activity (MOA) in lead borate glasses.^[1] In both cases, the medium crossed by linearly polarized light provokes a rotation of the polarization of light and the appearance of a related ellipticity. In turn, this ellipticity is due to a differential absorption of right and left circularly polarized light of the medium, called Natural Circular Dichroism (NCD) and Magnetic Circular Dichroism (MCD), respectively. Nonetheless, the phenomenological similarity between the two effects has different microscopic origins. This was not fully understood in the 19th century and has raised a lot of hopes about the possibility to control chiral systems with magnetic fields. Indeed, in 1848, Louis Pasteur tried to enantioselectively crystallize one of the two enantiomers of tartaric acid in a magnetic field.^[2] The experiments of Pasteur failed and the link between the two phenomena was discovered only in modern years.^[3,4]

The detailed symmetry-based description of NOA and MOA indicates that NOA originates from a nonlocal optical response of a medium that lack mirror symmetry, that is, a chiral system, while MOA originates from the breaking of time-reversal symmetry by the magnetization of the medium.^[5,6] This analysis was pushed forward to examine what would happen when a chiral magnetized system is probed by *unpolarized* light. It thus appears that when a chiral system is irradiated with unpolarized light, defined by its wavevector \mathbf{k} , in a magnetic field \mathbf{B} , light

absorption (A) can be enhanced or reduced (ΔA). This differential light absorption, that is, this dichroic signal, is triggered by the relative orientation of \mathbf{k} and \mathbf{B} and by the chirality of the system. This effect, which is equal in magnitude for two enantiomers but opposite in sign was named Magneto-Chiral Dichroism (MChD) (Figure 1).^[6] The same phenomenon can be observed in luminescence or in light refraction (Magneto-Chiral Birefringence).^[5,7] As opposed to NCD and MCD, MChD does not require a circularly polarized light source to be observed. As MCD, it is correlated to the magnetization of the system, either spontaneous or induced by the magnetic field.

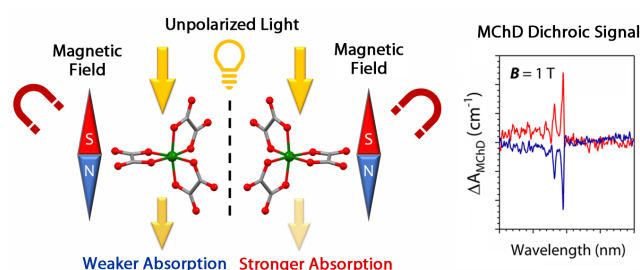


Figure 1. Schematic representation of the conditions needed to observe a MChD signal on a chiral molecule (left) and generic MChD dichroic signal resulting from the weaker and stronger absorption of light for a series of electronic transitions as a function of the enantiomer (right).

This minireview intends to demonstrate to the molecular chemistry community the interest in synthesizing molecular systems dedicated to the investigation of MChD. To do so, the basic concepts needed for any non-expert in the discipline to understand MChD are first presented. Then the experimental observations of MChD under different conditions (temperature, light wavelength, etc.) are illustrated to highlight the universality of this effect, the factors that seem to drive it, and its dependence with magnetization. Finally, we conclude with some perspectives on MChD and its possible relation with the appearance of homochirality of life on Earth.

2. Theoretical prediction of MChD

Historically, physics has developed by looking at effects that are linear in a given excitation. As shown in eq. 1, NCD and MCD are relevant to this approach, the former being proportional to \mathbf{k} and the latter to \mathbf{B} . Then, physics sought for effects beyond linearity. A relevant example is given by the study of non-linear optics, that studies the optical response of the medium with the power of the electric field borne by light. The understanding of the microscopic factors leading to such effects has boosted the synthesis of molecules with optimized hyperpolarizability by

molecular chemists and the development of corresponding photonic devices.^[8,9]

A second development came from the exploration of bilinear effects. Following this path, in 1982, Wagnière and Maier examined the simultaneous effect of \mathbf{k} and \mathbf{B} on the optical response of a medium (eq. 1). It appeared that a static magnetic field parallel to the direction of light propagation can produce a small change in the value of the absorption coefficient of a chiral molecule.^[3] This change was predicted to be independent of the polarization of the light beam and changes sign either upon replacing the chiral molecule by its enantiomer, or upon reversing the relative directions of magnetic field and light propagation vector. Baranova and Zel'dovich proposed a few years earlier a similar effect that manifests itself as a difference in refraction rather than absorption.^[7] Subsequently, in 1984, Barron and Vrbancich unified these phenomena in a unique context developing a microscopic model made of explicit expressions in terms of molecular property tensors and coined the terms Magneto-Chiral Dichroism (MChD) and Magneto-Chiral Birefringence (MChB) for the phenomenon observed in absorption and refraction, respectively.^[5,10] In more general terms, these two magneto-chiral effects can be described as two manifestations of Magneto-Chiral Anisotropy (MChA).^[6]

MChD can be formalized by expanding the frequency dependence (ω) of the absorption coefficient (ε) with \mathbf{k} and \mathbf{B} (eq. 1)

$$\varepsilon_{\pm}(\omega, \mathbf{k}, \mathbf{B}) = \varepsilon_0(\omega) \pm \alpha^{d/l}(\omega)\mathbf{k} \pm \beta(\omega)\mathbf{B} + \gamma^{d/l}(\omega)\mathbf{k} \cdot \mathbf{B} \quad (1)$$

where ε_0 is associated to the normal absorption of light at zero field, $\alpha^{d/l}$ to the NCD, β to the MCD, and $\gamma^{d/l}$ to the MChD, with d and l that refer to right- and left-handed medium, and \pm the right- and left-handed circularly polarized waves, respectively.^[11] Therefore, MChD is an effect that *i*) depends on the product $\mathbf{k} \cdot \mathbf{B}$, thus on the relative orientation of \mathbf{k} and \mathbf{B} , *ii*) depends on the handedness of the chiral medium, and *iii*) is independent of light polarization. It is important to highlight that the effect can be observed if a magnetization is generated or present in the medium. Accordingly, it can be observable in diamagnetic and paramagnetic media under magnetic field as well as in permanent magnets. Moreover, since the magnetization of the medium \mathbf{M} is taken into account in the above expression in the \mathbf{B} -dependent terms, highly magnetized systems like ferro- or ferrimagnets are expected to exhibit stronger effect.

When studying NCD or MCD, it is convenient to normalize the dichroic signal by the normal absorption, to obtain the so-called dissymmetry factors g , that for NCD reads:

$$g = \frac{A_+ - A_-}{\frac{1}{2}(A_+ + A_-)} = 2 \frac{\Delta A_{\pm}}{A} \quad (2)$$

where A_{\pm} is the absorption coefficient for right/left circularly polarized light. Analogously, the dissymmetry factor for MChD, also referred as asymmetry or anisotropy factor, can be defined as:

$$g_{\text{MChD}} = \frac{A(\mathbf{B}\uparrow\mathbf{k}) - A(\mathbf{B}\downarrow\mathbf{k})}{\frac{1}{2}(A(\mathbf{B}\uparrow\mathbf{k}) + A(\mathbf{B}\downarrow\mathbf{k}))} = 2 \frac{\Delta A_{\text{MChD}}}{A} \quad (3)$$

Symmetry arguments allow to predict the existence of MChD but do not give any information about its magnitude. An estimation of its magnitude was obtained by extending the Becquerel model^[7] for MOA and interpreting MChA a result of the Larmor procession in NOA.^[12] This simple model estimates that the strength of MChD is the product of the relative strength of NCD and MCD:

$$g_{\text{MChD}} = g_{\text{NCD}} \cdot g_{\text{MCD}} \quad (4)$$

It should be however noted that this approach is only valid if MOA is dominated by the so-called A terms (derivative-type shape of the dichroism), which is the case for all diamagnetic and many paramagnetic materials.

3. Experimental observations of MChD in magnetized systems

At the end of 1980s there was theoretical unanimity on the existence of MChD, but the first experimental observation of this effect was shown only in 1997. As suggested in the seminal work of Wagnière and Maier,^[3] Rikken and Raupach measured the difference in luminescence intensity of tris(3-trifluoroacetyl-*d/l*-camphorato)europium(III), $[\text{Eu}((d/l)\text{-tfc})_3]$, a chiral complex obtained by using a chiral ligand derived from the chiral pool, for light emitted parallel and antiparallel to the external magnetic field \mathbf{B} .^[6] Taking advantage of the strong magnetic-dipole character and the strong MCD response of the ${}^5D_0 \rightarrow {}^7F_{1,2}$ luminescent transitions of Eu^{III} (Figure 2a) they observed a magneto-chiral signal for both ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions (Figure 2). For the two enantiomers, the dissymmetry factors have the same magnitude but are opposite in sign. The expected linear magnetic field dependence of g_{MChD} for this paramagnetic system was also shown (inset of Figure 2). These results thus demonstrated for the first time the existence of MChD and its enantioselectivity.^[6]

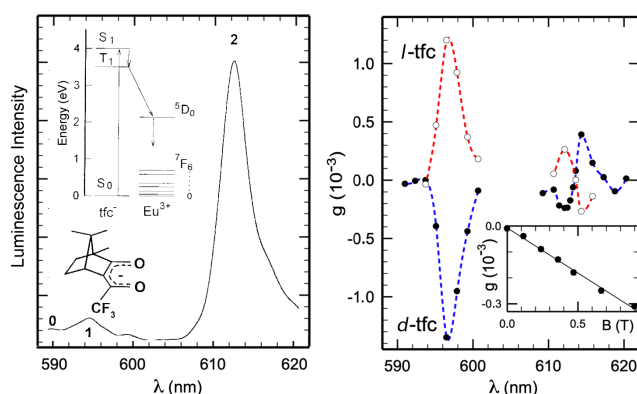


Figure 2. Luminescence spectra of $[\text{Eu}((d/l)\text{-tfc})_3]$ dissolved in deuterated dimethyl sulphoxide ($\lambda_{\text{exc}} = 350 \text{ nm}$) with peaks labelled with the J subscript of the final 7F_J level (left). Magneto-Chiral luminescence anisotropy of $[\text{Eu}((d/l)\text{-tfc})_3]$ (5% w/w) as a function of luminescence wavelength (filled symbol represents the $[\text{Eu}((d)\text{-tfc})_3]$ and open symbols the $[\text{Eu}((l)\text{-tfc})_3]$ enantiomer (right). Inset shows the magnetic field dependence of the g dissymmetry factor. Adapted with permission from ref. [6]. Copyright 1997, Macmillan Publishers Limited.

It should be noted that the shapes of the two magneto-chiral bands are different and that the most intense luminescence transition is not the one associated to the highest dissymmetry factor.

More recently, Taniguchi and coworkers used a similar approach to investigate MChD through visible light emission in pairs of *nona*- et *octa*-coordinated lanthanide chiral complexes formulated as $[\text{Ln}(\text{L}^{\text{SS/RR}})_3]\text{X}_3$ ($\text{Ln} = \text{Tb}^{\text{III}}, \text{Eu}^{\text{III}}$; $\text{L}^{\text{SS/RR}} = \text{N}, \text{N}'\text{-}(\text{X}, \text{X})\text{-bis}(1\text{-phenylethyl})\text{-2,6-pyridine carboxamide}$; $\text{X} = \text{CF}_3\text{SO}_3^-, \text{ClO}_4^-$) and $[\text{Ln}((d/l)\text{-tfc})_3(\text{phen})]$ ($\text{Ln} = \text{Tb}^{\text{III}}, \text{Eu}^{\text{III}}$; $\text{phen} = \text{phenantroline}$).^[13] The intensity of MChD observed for specific *f-f*

electronic transitions has been compared for the two lanthanide ions (Tb^{III} versus Eu^{III}) and for the different coordination geometry (*nona* versus *octa*). Stronger MChD signals were observed for the Tb^{III} complexes when compared to the Eu^{III} ones, and for the nonacoordinated complex when compared to the octacoordinated ones. They correlated the former observation with the larger magnetic moment of Tb^{III} , which is associated to a ground state with $J \neq 0$, and the latter with the smaller inversion symmetry breaking at the lanthanide center.^[13] With this study, Taniguchi and coworkers provided one of the rare systematic investigations of MChD in lanthanide complexes reported so far and proposed some design criteria for MChD maximization.

As recalled above, the relation between the Einstein's coefficients in radiative processes tells us that if MChD is observed in emission, the same phenomenon should also be observed in birefringence or absorption. Indeed, using an interferometric method that canceled any linear effects, Wagnière et al. have measured the magneto-chiral birefringence of diamagnetic chiral molecules as pure liquids^[14] or in solution (including proline in water), and of diamagnetic chiral crystals.^[15] Right after, Rikken and Raupach selected α - $NiSO_4 \cdot 6H_2O$ as a good candidate for the observation of MChD in absorption.^[11] This compound undergoes spontaneous resolution as it crystallizes as a conglomerate either in the $P4_12_12$ or $P4_32_12$ enantiomorphic space groups. In the solid state the achiral building blocks form left-handed ($P4_12_12$) or right-handed ($P4_32_12$) helices of $[Ni(H_2O)_6]^{2+}$ complex cations hydrogen bonded to sulfate anions.^[16] In addition, the single-crystals can be easily separated because α - $NiSO_4 \cdot 6H_2O$ has a sizable NCD response. Accordingly, large single crystals with unique handedness of this compound were used to first demonstrate MChD in the solid-state through visible light absorption. This experiment provides a quantitative evaluation of the magnitude of this effect by comparing the intensity of the MChD signal with the absorption coefficient (A) of the material.^[11] The observed MChD dissymmetry factor was in agreement with the order of magnitude ($10^{-3} T^{-1}$) predicted by eq. 4 although the line-shape was not reproduced. This is explained by the fact that the MOA of this material is not dominated by A -terms, evidencing a limitation of the model.^[11]

The microscopic theory of MChD defines its dependence on the handedness of the enantiomer, the direction of the light propagation vector, as well as the intensity of the applied magnetic field (or the magnetization of the system) and its direction. Furthermore, it highlights that electromagnetic radiations of different frequencies can interact with a chiral magnetized medium to provide MChD. The microscopic theory of MChD also states that the relative MChD effect, e.g. the dissymmetry factor g_{MChD} , increases when the typical length of the chiral object matches the wavelength of the electromagnetic radiation used to probe the system.^[5,10] Accordingly, for a chiral center at the atomic scale, like a chiral carbon atom or a helical tris(bidentate) metal complex, X-rays appear as the best suited radiations, whereas, for millimetric ferromagnetic helices, microwaves are more adapted to maximize the effect.^[17]

Following these predictions, investigations were undertaken to demonstrate that MChD can be observed in other regions of the electromagnetic spectrum.

A first seminal work aimed at observing MChD through hard X-ray absorption in molecular compounds was performed by Galán-Mascarós et al.^[18] Paramagnetic enantiopure heterometallic complexes of formula $\{Tb[Ni(L/D-$

proline) $\}_2\}(\text{NO}_3)_2(\text{ClO}_4)$ were investigated by X-ray Absorption Near Edge Spectroscopy (XANES) at the $L_{2,3}$ -edges of Tb and K edge of Ni. They observed for the first time a MChD signal at room temperature related to the L_2 XANES edge of terbium whose intensity was ca. 1% of the total absorption. Surprisingly, no MChD was observed at the L_3 edge of the same metal and at the Ni K edge.^[18]

Sessoli et al. investigated the properties of enantiopure helical molecular chains formulated as $[M^{II}(\text{hfac})_2\text{NITPhOMe}]$ ($M^{II} = \text{Co}, \text{Mn}$; hfac = hexafluoro-acetylacetonato; NITPhOMe = 2-(4-methoxyphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-1,3-oxide) obtained by spontaneous resolution in right and left-handed configurations (space groups $P3_1$ or $P3_2$ respectively) by hard X-ray light absorption at the K-edge of the metal present in these systems.^[19] The magnetic properties of these compounds are dominated by a strong exchange coupling between the paramagnetic metal ions and the unpaired electron of the bridging radical ligand based on the nitronyl-nitroxide (NIT) moiety. While the Mn^{II} behave as a 1D Heisenberg ferrimagnet at low temperature due to the lack of an orbital contribution to the magnetic moment, the Co^{II} derivative shows slow relaxation of the magnetization due to the significant orbital moment typical of its electronic configuration in an octahedral coordination environment.^[19]

The XANES, XNCD, XMCD and XMChD spectra for the Co^{II} and Mn^{II} derivatives are reported in Figure 3. The comparison between the results of the XMChD spectra obtained for the two compounds, evidences that the Co^{II} derivative shows a robust MChD signal at the pre-edge, ca. 0.2% of the corresponding normalized absorption, while for the Mn^{II} compound the effect is very weak. This difference has been attributed to the important orbital contribution to the magnetic moment of the Co^{II} ion, which is instead vanishing for Mn^{II} .^[19] XMChD and XMCD signals both follow a magnetic field dependence that closely resemble the magnetization curve, thus evidencing the proportionality of both phenomena with the magnetization of the system.^[19,20] The XMChD intensity does not follow the model reported in eq. 4, further underlining its limitation in predicting the intensity and shape of MChD.

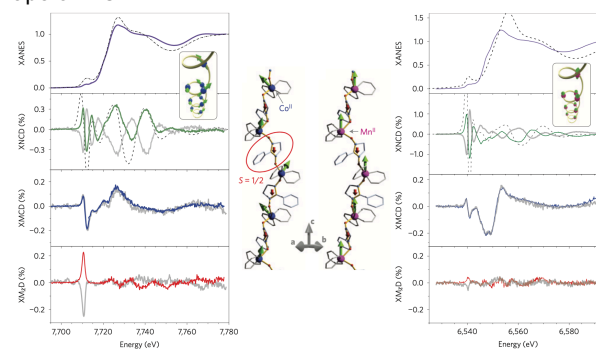


Figure 3. Normalized XANES spectra at the K-edge of Co (left) and Mn (right) measured at $B = 3 \text{ T}$ and $T = 5 \text{ K}$. The dichroic contributions are expressed as the percentage of the edge jump in the absorption and are reported for two opposite enantiomers, one in color and the other in pale grey, for graphical clarity. The dashed black lines correspond to the calculated XANES and XNCD for the $P3_1$ enantiomer, whose helicity is visible in the schematic structure drawn in the inset, with arrows representing the non-collinear spin structure of the molecular helix. A view of the molecular structures of the $[M^{II}(\text{hfac})_2\text{NITPhOMe}]$ compounds is also reported in the middle. Adapted with permission from ref. [19]. Copyright 2014, Macmillan Publishers Limited.

MChD was thus observed using a highly energetic radiation as hard X-rays. Lower energy radiations, such as microwaves, were recently proved to be also suitable to detect this effect. Tomita and coworkers reported on the observation of MChD at X-band microwave radiations for a metamolecule consisting of a copper chiral coil and a ferrite rod with a millimeter-scale helicity well-adapted to the selected radiation wavelength.^[21] The cross-effect between chirality and magnetism is here “fictitious” because the electronic interactions between the chirality and the magnetic properties of the copper and the ferrite components are not intrinsic. However, they clearly observed a change of the intensity at the resonant frequency of the system when applying a static magnetic field varying from 1 mT up to 200 mT.^[21] Although observed in a metamolecule and sustained by the strong magnetic response of ferrites at low magnetic fields, this report demonstrates once again the universality of MChD, posing the basis for the observation of such an effect in a purely molecular chiral system with microwave radiation.

4. MChD in Molecular Magnets

MChD is directly related to the magnetization of the system. In the systems described so far, a weak magnetization was induced by applying an external magnetic field. The observation and investigation of MChD in a magnetically ordered material that shows retention of the magnetization has two fundamental interests: *i)* magnetic ordering is expected to enhance the intensity of the signals and allow an easy observation at temperatures higher than those at which the phenomenon is typically observed for paramagnets at ordinary magnetic fields; *ii)* it can be in principle used for the optical readout of magnetic data stored in these materials using an unpolarized light source instead of a circularly polarized one. Nonetheless, introducing chirality into molecule-based magnets appeared as a synthetic challenge.^[16] This was taken up using different synthetic strategies in two of the most studied families of molecule-based magnets, oxalate-based networks and Prussian Blue Analogues (PBA).

In 2008, an enantiopure chiral oxalate-bridged 2D coordination polymer formulated as $[\text{N}(\text{CH}_3)(n\text{-C}_3\text{H}_7)_2(\text{X})\text{-sec-C}_4\text{H}_9][\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]$ ($\text{X} = \text{S}, \text{R}$) (Figure 4) was obtained by enantioselective self-assembly, using a resolved chiral quaternary ammonium cation $[\text{N}(\text{CH}_3)(n\text{-C}_3\text{H}_7)_2(\text{X})\text{-sec-C}_4\text{H}_9]^+$. As demonstrated by NCD, during the self-assembly process the cation imposes the absolute configurations of the helical tris(bidentate) Cr^{III} and Mn^{II} metal centers of the 2D anionic layers.^[22] In this material, super-exchange magnetic interactions between metal ions bridged by oxalate anion leads to a ferromagnetic ordering below a Curie temperature of 7 K.

The MChD spectrum of the two enantiomers revealed that the effect was dominated by the Cr^{III} $d\text{-}d$ transitions. By following the temperature dependence of the MChD signal observed at $\lambda = 615$ nm (Figure 4), a dramatic increase of the MChD signal when passing from the paramagnetic phase to the ferromagnetic one was observed.^[22]

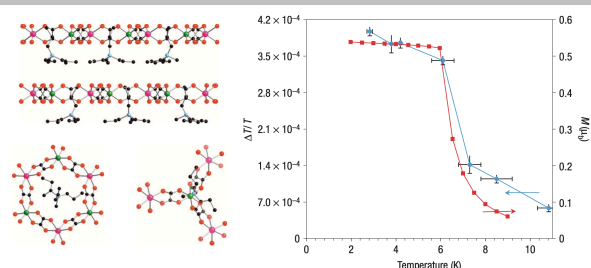


Figure 4. View of the molecular and crystal structure of $[\text{N}(\text{CH}_3)(n\text{-C}_3\text{H}_7)_2(\text{X})\text{-sec-C}_4\text{H}_9][\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]$ (left) and temperature dependence of the MChD of measured at 615 nm compared to field-cooled magnetization data (right). Adapted with permission from ref. [22]. Copyright 2008, Macmillan Publishers Limited.

This evidenced for the first time the crucial effect that magnetic ordering within chiral molecular magnets can have on the observation of strong MChD. It also paved the way for the development of chemical approaches oriented towards the enhancement of the ordering temperature in these materials in order to further exploit their MChD properties.^[23]

Following this idea, we have recently selected $[\text{Mn}^{\text{II}}(\text{X-pnH})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{R}$; $\text{pn} = 1,2\text{-propanediamine}$), a chiral PBA where the chirality is introduced in the material by adding a chiral coligand to the usual reactants needed to form PBA.^[24] Using resolved 1,2-propanediamine, it is possible to generate enantiomorphic crystals (space group $P2_12_12_1$) of a compound that has a remarkable ferrimagnetic ordering temperature of 38 K due to the superexchange coupling between Mn^{II} and Cr^{III} ions mediated by the cyanide ligand (Figure 5).^[25]

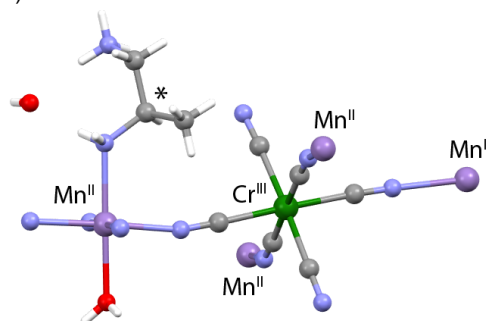


Figure 5. View of the molecular moiety of $[\text{Mn}^{\text{II}}(\text{X-pnH})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$ with cyanido bridge between Mn^{II} and Cr^{III} ions highlighted. Colour codes: violet, Mn; green, Cr; blue, N; red, O; gray, C; white, H. The asterisk indicates the stereogenic centre on the ligand. Adapted with permission from ref. [24]. Copyright 2019, American Chemical Society.

It should be noted that in this compound the metal centers are not chiral (Figure 5), contrarily to the previously described $[\text{N}(\text{CH}_3)(n\text{-C}_3\text{H}_7)_2(\text{sec-C}_4\text{H}_9)[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)_3]$ system. However, the attribution of the electronic transitions observed in the absorption spectra at low temperature (Figure 6) allowed to demonstrate that the chiral coligand coordinated to the Mn^{II} center strongly influences the electronic transitions associated to this ion so that they actually display strong MChD signals despite the negligible orbital contribution to the magnetic moment of Mn^{II} (Figure 6). On the contrary, the Cr^{III} center, which is not coordinated to the chiral coligand shows vanishingly small MChD.^[24]

A similar observation has been made by Taniguchi and coworkers through the investigation of the MChD response of a chiral heterometallic system formulated as $[\text{Cu}^{\text{II}}((1\text{X},2\text{X})\text{-chxn})_2]_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{S}; \text{R}, \text{R}; \text{chxn} = 1,2\text{-diamino-cyclohexane}$).^[26] A weak MChD signal was observed for the electronic $d-d$ transition of the Cu^{II} ion coordinated to the chiral chxn ligand, while the $[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ moiety do not provide any detectable MChD response.^[26] These observations confirm the non-local influence of the chiral center onto the MChD and set a limit to the distance between the chiral and magnetic centers for observing MChD in the visible range. Moreover, from these experiments, it appears that the orbital contribution that plays a central role in the pre-edge signal in the X-ray region (Figure 3), e.g. for electronic transitions between core state and valence state, seems not to be crucial for observing MChD associated to electronic transitions between valence states.

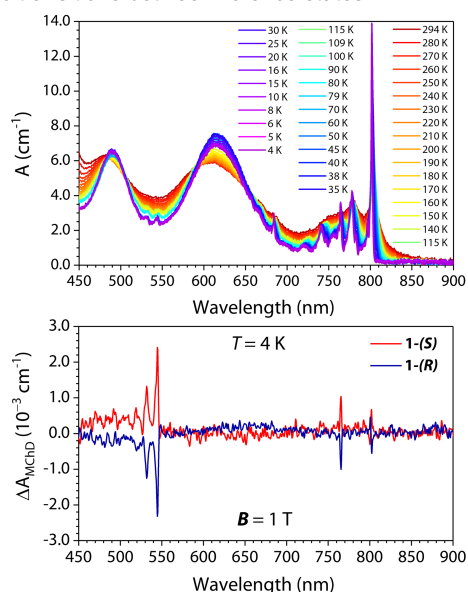


Figure 6. Temperature variation (see legend) of the single-crystal absorption spectrum of $[\text{Mn}^{\text{II}}(\text{X-}pn\text{H})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ (top) and MChD signals detected at $T = 4 \text{ K}$ and $B = 1.0 \text{ T}$ for both enantiomers (down). Adapted with permission from ref. [24]. Copyright 2019, American Chemical Society.

The temperature and magnetic field dependences of the strongest MChD signals intensity for both enantiomers of $[\text{Mn}^{\text{II}}(\text{X-}pn\text{H})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ were investigated up to 80 K and 1.5 T, respectively. This evidenced that MChD closely follow the temperature and magnetic field dependence of the magnetization and that strong MChD signals can be observed up to the ordering temperature of the material (38 K).^[24] With this study the observation of MChD in an ordered magnet has been pushed from 7 K to 38 K, an important step toward the use of MChD for the optical readout of magnetic data using unpolarized light at viable temperatures.

5. Conclusions and Outlook

MChD is a fascinating manifestation of light-matter interaction typical of chiral magnetized systems. While in inorganic materials the absence of centrosymmetry is totally dependent on their serendipitous crystallization in chiral space groups by spontaneous resolution, in molecular materials chirality can be introduced and controlled in a rational manner.

The strategy of rationally introducing chirality in molecular materials has been used in many fields, for example that of conducting molecular materials to improve the conducting properties through modulation of the structural disorder of some racemic systems.^[27] Chirality has been also introduced to investigate magneto-chiral anisotropy in electric transport.^[28]

Instead, a similar approach oriented at introducing chirality in magnetic molecular materials with the purpose of investigating and understanding the microscopic origins of MChD is so far scarce and limited to very few examples. A first reason is the experimental challenges that must be taken up to efficiently detect this effect. They were only recently addressed with homemade setups relying on multichannel phase sensitive detection of absorption spectra in alternating magnetic fields.^[29]

A second reason lies in the synthetic challenge towards enantiopure magnetic systems. The study of the chiral PBA described above highlights that the chemical strategies developed by chemists working on molecular magnetism with the scope of enhancing the ordering temperatures in magnetic exchange coupled systems or the magnetic anisotropy of system showing slow relaxation of the magnetization, can be translated into chiral materials with a different scope: exploring and understanding the microscopic parameters that govern this scarcely investigated manifestation of light-matter interaction.

Rational studies into this direction will be highly beneficial for a future technological application of this effect, that is, the use of unpolarized light to probe the magnetic information stored in these materials.

At the same time, they will be beneficial to answer one universal unsolved question: why life on Earth is homochiral? MChD has been proposed as a possible mechanism for the emergence of homochirality of life on Earth^[1] on the basis of its enantioselective nature and the implication of two physical entities that are ubiquitous in our universe: unpolarized light emitted from stars, and magnetic fields at the core of some planets, including Earth, and neutron stars.^[30] The enantioselective nature is related to the magneto-chiral influence through “true chirality”, as defined by L. D. Barron,^[31,32] that is associated to a static magnetic field collinear with an unpolarized light beam. A crucial experiment confirmed this possibility: the photochemical enantiomerisation of tris(oxalato)chromate(III) studied under magnetic field demonstrated the generation of an enantiomeric excess (e.e.) by irradiation of a racemic mixture by unpolarized light aligned with the magnetic field, the sign of the e.e. being determined by the relative orientation of the light and the magnetic field.^[33] In addition, MChD has been observed in purely organic compounds^[34] based on porphyrins^[35] and phthalocyanines^[36] by Ishii and coworkers, evidencing the role of the high angular momentum of π conjugated systems for the observation of a strong MChD in these compounds. Moreover, theoretical calculations have confirmed the existence of significant MChD in amino acids^[37] whereas magneto-chiral birefringence was observed in a solution of enantiopure proline dissolved in water.^[15]

Although we are still far from answering the question of the origin of homochirality of life, these results suggest that MChD merits consideration in this discussion, while rational chemical studies to MChD investigations in Molecular Materials might open important perspectives for a potential technological role of this effect.

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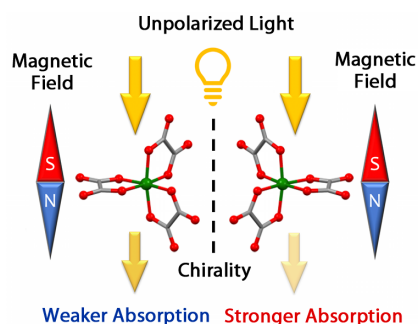
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This minireview provides a description of Magneto-Chiral Dichroism, an unconventional manifestation of light-matter interaction that can be observed in chiral magnetized systems. By recalling the main results obtained so far, we highlight the challenges opened for the molecular chemistry community interested in investigating this fascinating effect with potential technological applications and implications in the emergence of homochirality of life on Earth.