Magneto-Chiral Anisotropy: From Fundamentals to Potential Applications

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Outline

- Symmetry
- Ingredients for Magneto-Chiral Effects
- Electrical Magneto-Chiral Anisotropy
- Optical Magneto-Chiral Anisotropy
- Conclusions

Symmetry

- **Continuous symmetries (Noether theorem):**

Time-translation invariance, $t \rightarrow t+\Delta t \Leftrightarrow$ *Energy conservation*

Translational invariance, $r \rightarrow r+\Delta r \Leftrightarrow$ *Momentum conservation*

Rotational invariance, $\varphi \rightarrow \varphi+\Delta\varphi \Leftrightarrow$ *Angular momentum conservation*

- **Charge, Parity, Time reversal (CPT) symmetry:**

Charge conjugation, **C**, $q \rightarrow -q$ *(matter → anti-matter)*

Parity transformation, **P**, $r \rightarrow -r$ *(mirror image)*

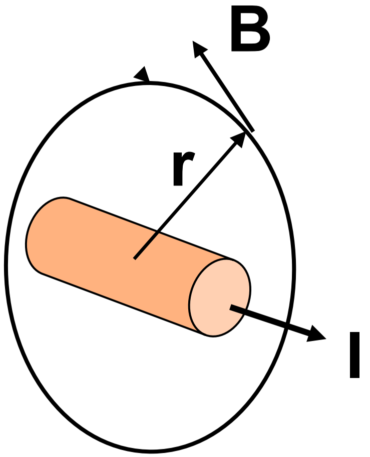
Time-reversal, ***T***, $t \rightarrow -t$ (*play movie backwards*)

CPT symmetry of a Magnetic Field *B*

$$\mathbf{B} = \frac{1}{4\pi\varepsilon_0}\frac{2\mathbf{I}\times\mathbf{r}}{r^2}$$

$$\mathbf{I} = qN\frac{\partial\mathbf{r}}{\partial t}$$

$$\mathbf{B} = \frac{qN}{4\pi\varepsilon_0}\frac{2\frac{\partial\mathbf{r}}{\partial t}\times\mathbf{r}}{r^2}$$



- **CPT symmetry:**

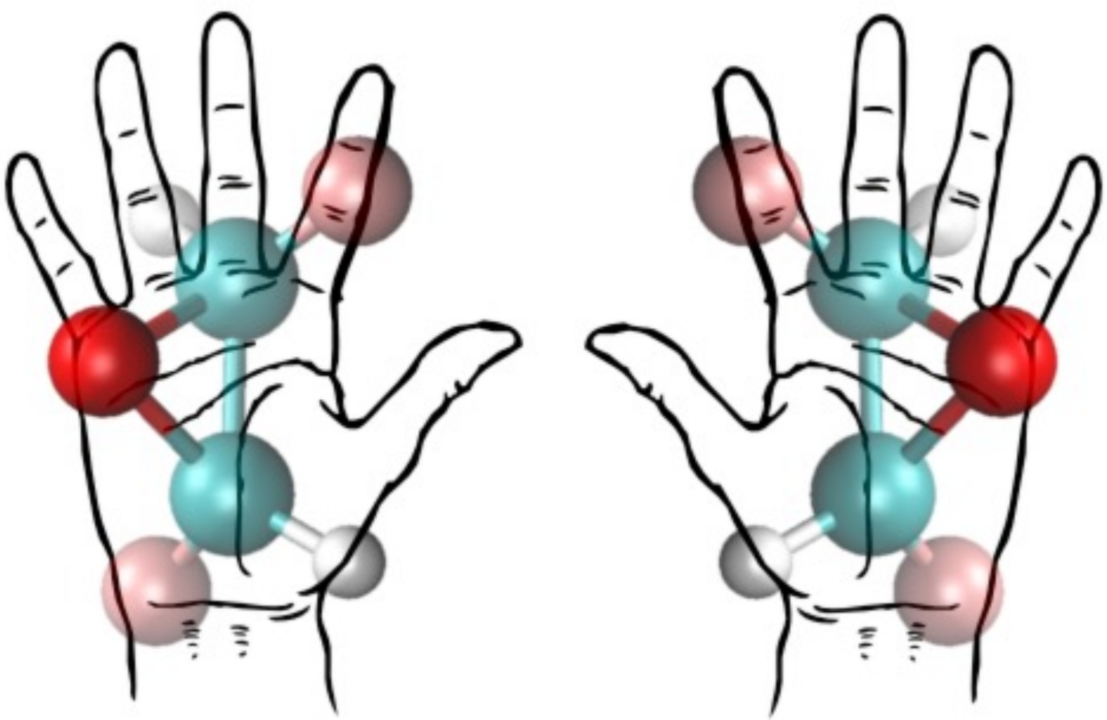
Charge conjugation, **C**, ***B*** $\rightarrow -$ ***B*** *(holes* $\rightarrow$ *electrons)*

Parity transformation, **P**, ***B*** $\rightarrow$ ***B*** *(does not change)*

Time reversal, ***T***, ***B*** $\rightarrow -$ ***B*** *(electrons flowing in opposite directions)*

Magnetic field is a time-odd pseudo-vector

Chirality



A system is called chiral when it exists in two non-superimposable forms (enantiomers) that can only be interconverted by a parity operation

Chirality breaks parity (or mirror) symmetry

CPT symmetry of a Physical Entities

		C	P	T
energy	E	+	+	+
charge	q	-	+	+
polarization	$\boldsymbol{P}$	-	-	+
force	$\boldsymbol{F}$	+	-	+
magnetization	$\boldsymbol{M}$	-	+	-
light wavevector	$\boldsymbol{k}$	+	-	-
electrical current	$\boldsymbol{I}$	-	-	-
magnetic field	$\boldsymbol{B}$	-	+	-
electric field	$\boldsymbol{E}$	-	-	+
linear momentum	$\boldsymbol{p}$	+	-	-
angular momentum	$\boldsymbol{L}$	+	+	-

Magneto-Chiral Effects

Magnetic Fields *B* → **Breaking of <u>time-reversal</u> symmetry** **T**

Chirality → **Breaking of <u>space-reversal</u> symmetry**

Third ingredient → **Breaking of <u>space-reversal</u> (parity) symmetry** **P**

Magneto-Chiral Anisotropy

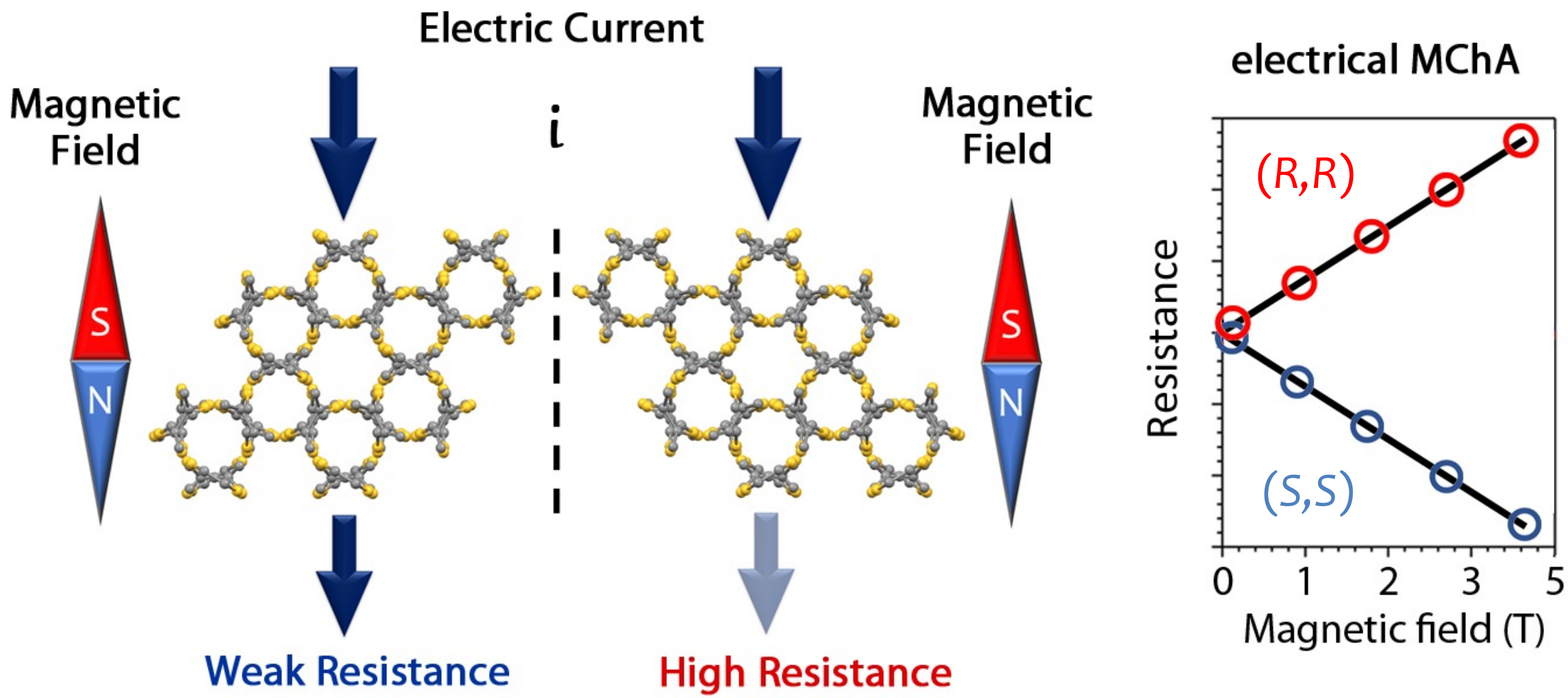
Transport: Electrical or thermal conductivity, sound propagation, dielectric displacement (**eMChA**)

Optics: light absorption or emission for all energies of the electromagnetic spectrum (**oMChA**)

electrical Magneto-Chiral Anisotropy, eMChA

Chirality + Electric Current + Magnetic Field

Differential resistance of Chiral Molecular Conductors in Magnetic Field



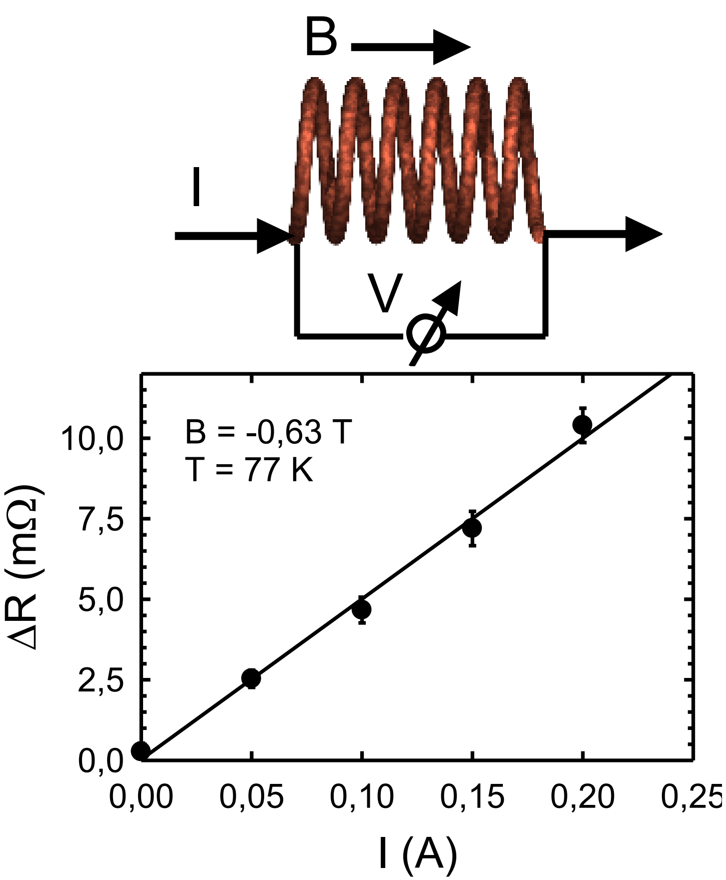
$$R(\mathbf{B},\mathbf{I})^{D/L} = R_0(1+\beta B^2 + \Omega^{D/L}\mathbf{B}\cdot\mathbf{I})$$

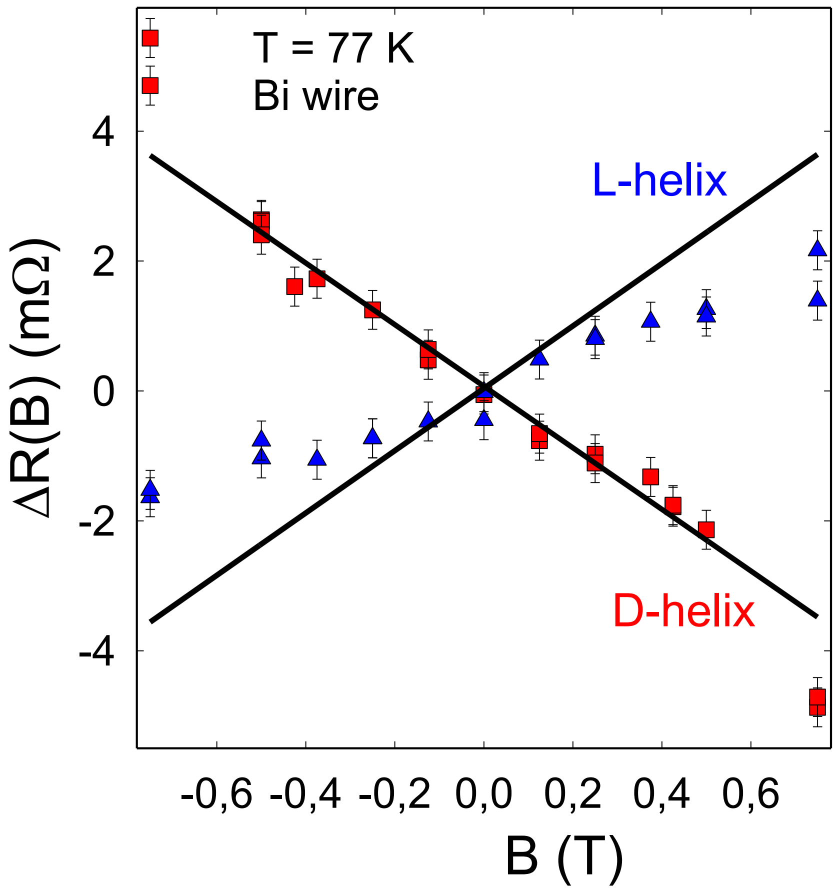
$$\frac{R(\mathbf{B},\mathbf{I})^{D/L} - R(-\mathbf{B},\mathbf{I})^{D/L}}{R_0} = 2\Omega^{D/L}\mathbf{B}\cdot\mathbf{I}$$

G.L.J.A. Rikken, J. Fölling, P. Wyder, *Phys. Rev. Lett.* **2001**, *87*, 236602

electrical Magneto-Chiral Anisotropy, eMChA

Bi solenoid
L and D helix



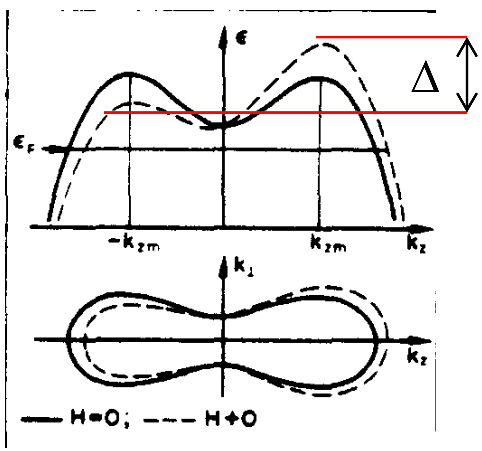


G.L.J.A. Rikken, J. Fölling, P. Wyder, *Phys. Rev. Lett.* **2001**, *87*, 236602

electrical Magneto-Chiral Anisotropy, eMChA

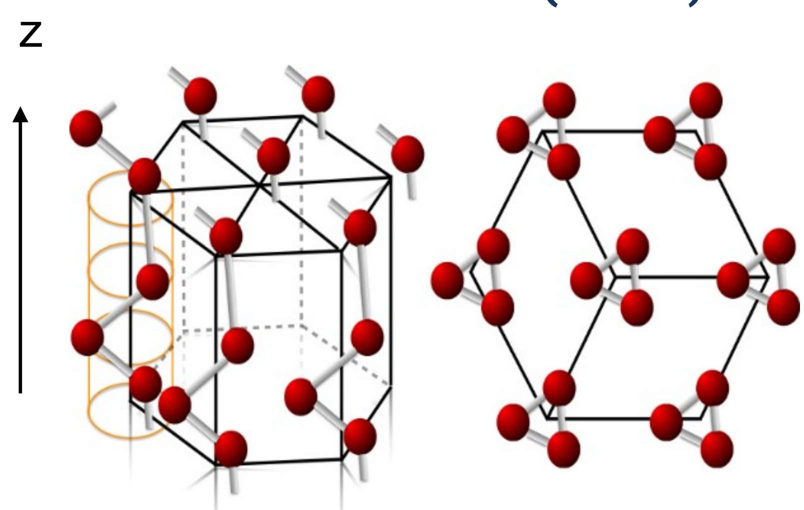
B // z : no k-linear effects

B ⊥ z : k-odd splitting

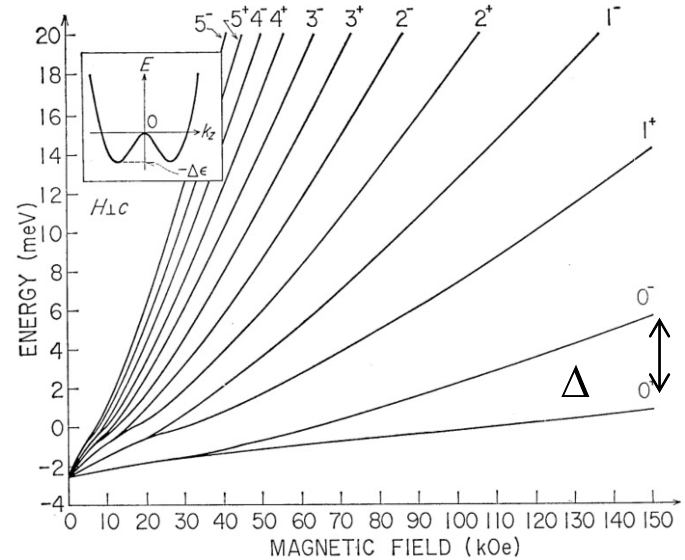


Anzin et al, Solid State Comm. **8**, 1773 (1970)

Tellurium wires (chiral)



$P3_121$-D^4_3



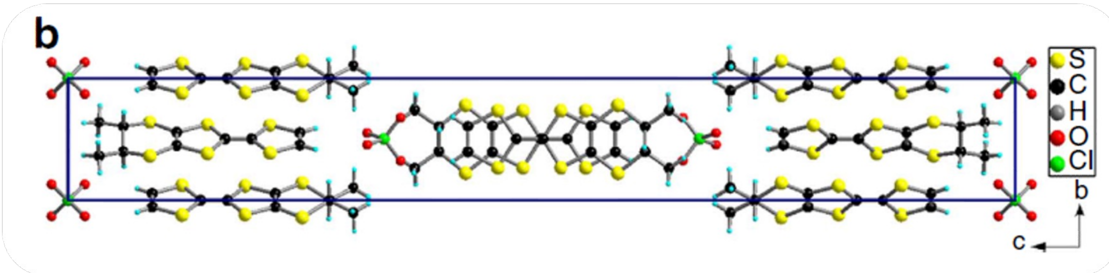
Theory: $\gamma^{D/L}_{xxxx} = 6\ 10^{-10}\ \frac{m^2}{TA}$

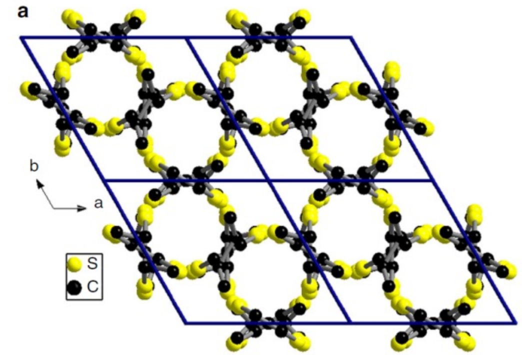
Experiment: $\gamma^{D/L}_{xxxx} = 2\ 10^{-9}\ \frac{m^2}{TA}$

G.L.J.A. Rikken and N. Avarvari, *Phys. Rev. B* **2019**

electrical Magneto-Chiral Anisotropy, eMChA

eMChA in the chiral molecular conductors: (*S*,*S*)- or (*R*,*R*)-$[DM\text{-}EDT\text{-}TTF]_2ClO_4$





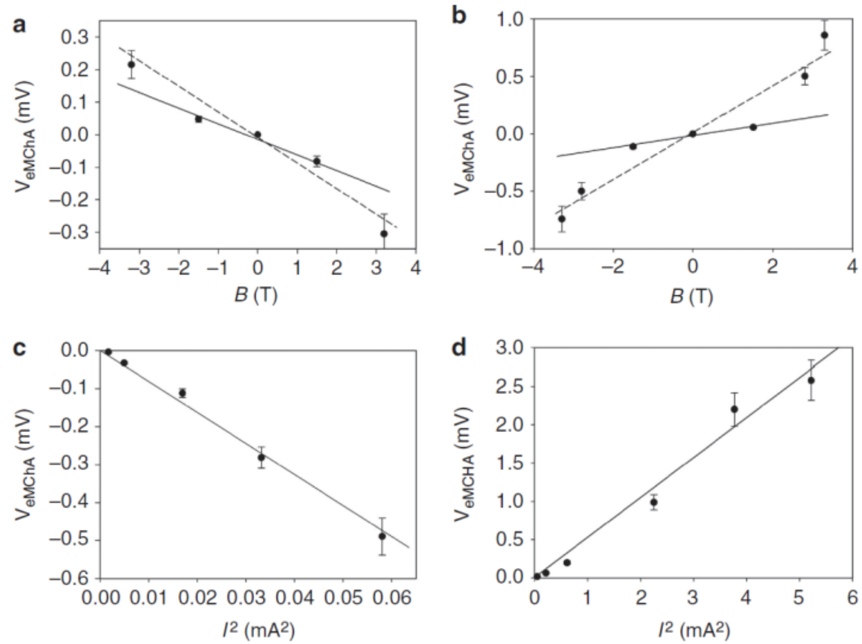
eMChA

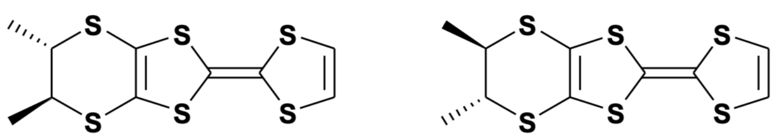
$$\frac{\Delta R}{R} = 2\gamma^{D/L}\mathbf{B}\cdot\mathbf{I}$$

eMChA parameters

(*S*,*S*)-γ (T^{-1} A^{-1}) = +6 × 10^{-2}

(*R*,*R*) -γ (T^{-1} A^{-1}) = -6 × 10^{-2}





dimethyl-ethylenedithio-tetrathiafulvalene

F. Pop, P. Auban-Senzier, E. Canadell, G. L. J. A. Rikken, N. Avarvari, *Nat. Commun.* **2014**, 5, 3757

electrical Magneto-Chiral Anisotropy, eMChA

Summary of eMChA

	Material	$\Delta R/R$ [m²/TA]	remark
*	Triglycine sulfate	3.10^{-5}	dielectric
*	Rochelle salt	3.10^{-6}	dielectric
	Te	5.10^{-8}	200 K, semiconduc.
	DM-TTF-ClO_4	10^{-10}	Room *T*
	WS_2	10^{-10}	Low *T*
	$CrNb_3S_6$	10^{-12}	Low *T*
	MnSi	2.10^{-13}	Low *T*
	SW-Carbon Nano Tubes	10^{-14}	Low *T*

Other chiral semi-conductor candidates:

Se, α-HgS, π-SnS, In_2Se_3, $AlInSe_3$, $GaInSe_3$, α- Al_2S_3, $BaSi_2$, $CrSi_2$, $MoSi_2$, WSi_2

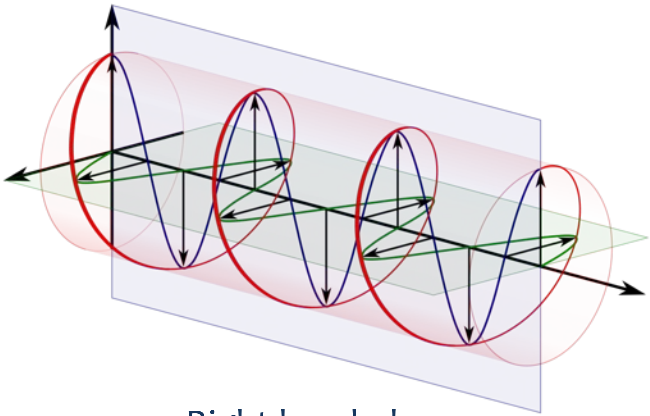
* G. L. J. A. Rikken, N. Avarvari, *Nat. Commun.* **2022**, 13, 3564 G. L. J. A. Rikken, N. Avarvari, *Phys. Rev. B* **2022**, 106, 224307

Magneto-Chiral Effects in Optics

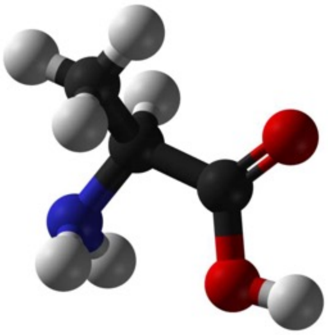
Chirality	→	Breaking of space-reversal symmetry	
Magnetic Fields *B*	→	Breaking of time-reversal symmetry	T
Light wavevector *k*	→	Breaking of space-reversal (parity) symmetry	P

Interaction of Chiral Systems with Circularly Polarized Light

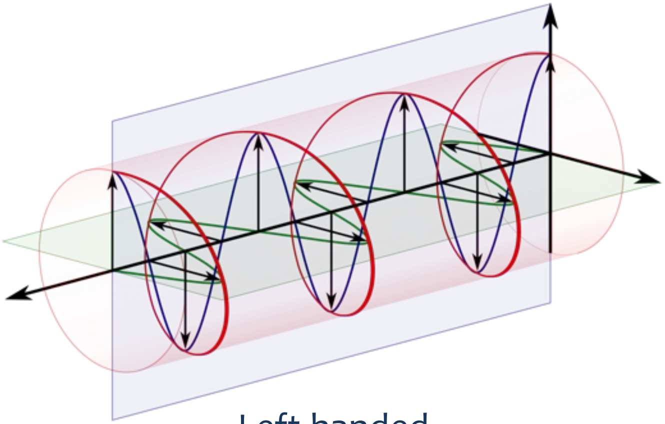
Natural Optical Activity: Natural Circular Dichroism (NCD)



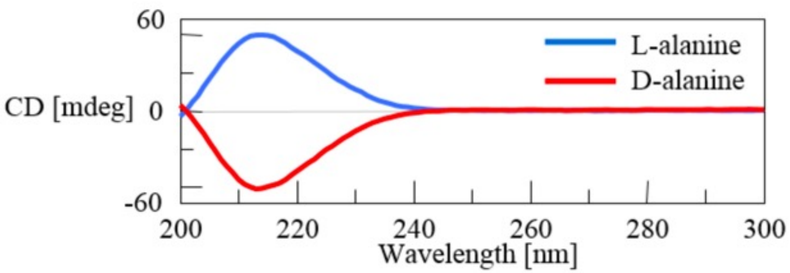
Right-handed circular polarized light



L-alanine



Left-handed circular polarized light

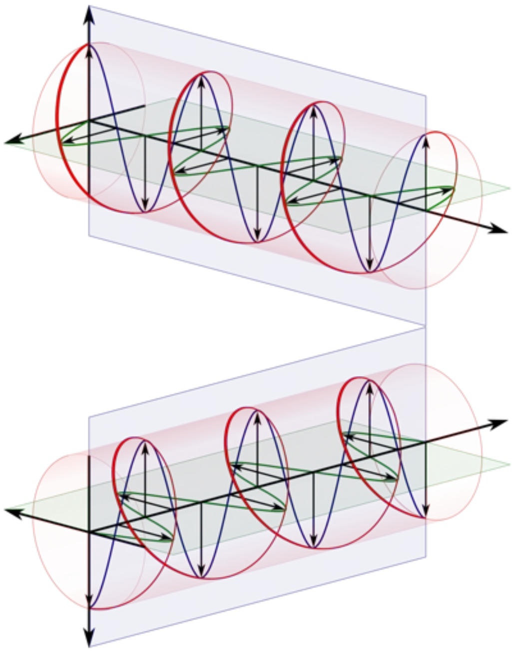


$$\varepsilon(\lambda, \boldsymbol{k}) = \varepsilon_0(\lambda) \pm \alpha^{d/l}(\lambda)\boldsymbol{k}$$

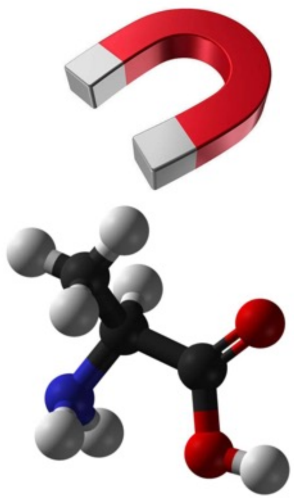
Breaking of space-reversal symmetry by chirality leads to natural optical activity

Interaction of a system with Circularly Polarized Light and Magnetic Field

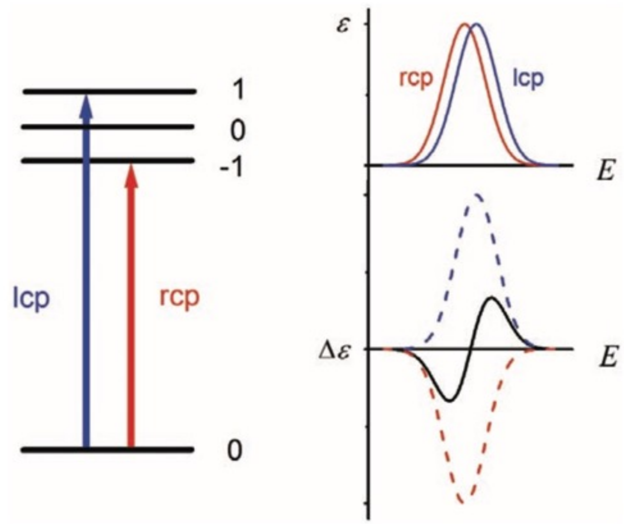
Magnetic Optical Activity: Magnetic Circular Dichroism (MCD)



Magnetic Field



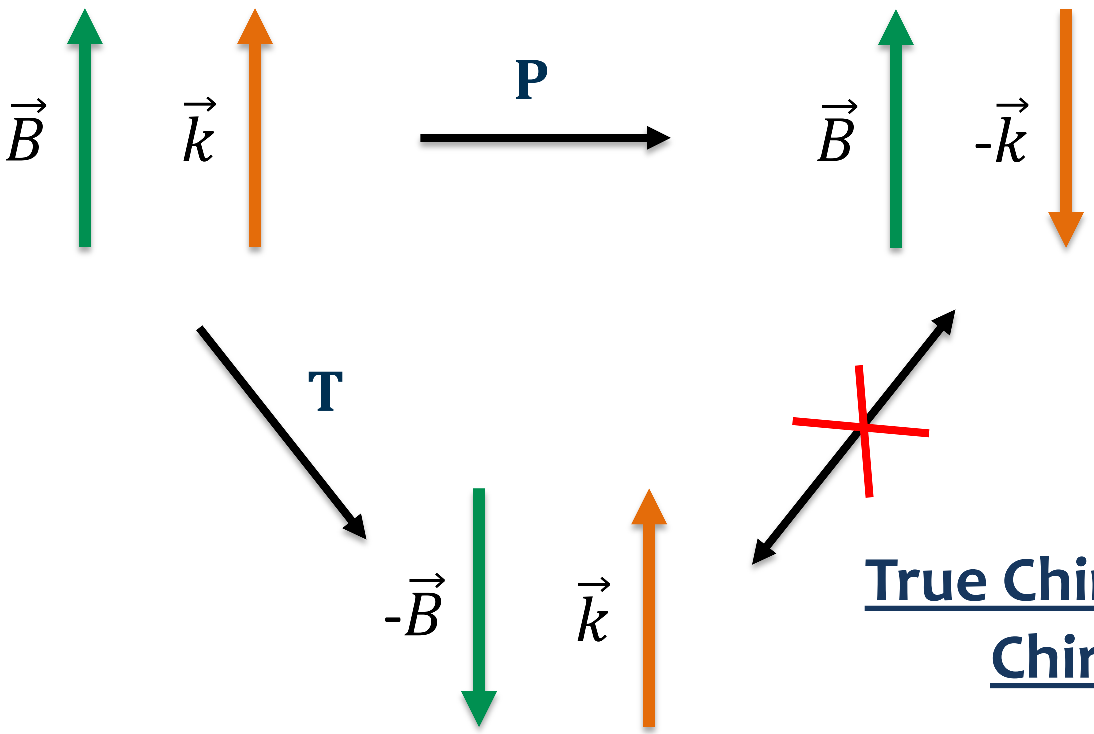
chiral or not



$$\varepsilon(\lambda, \boldsymbol{B}) = \varepsilon_0(\lambda) \pm \beta(\lambda)\boldsymbol{B}$$

Breaking of time-reversal symmetry by magnetic fields leads to magnetic optical activity

Optical Magneto-Chiral Anisotropy



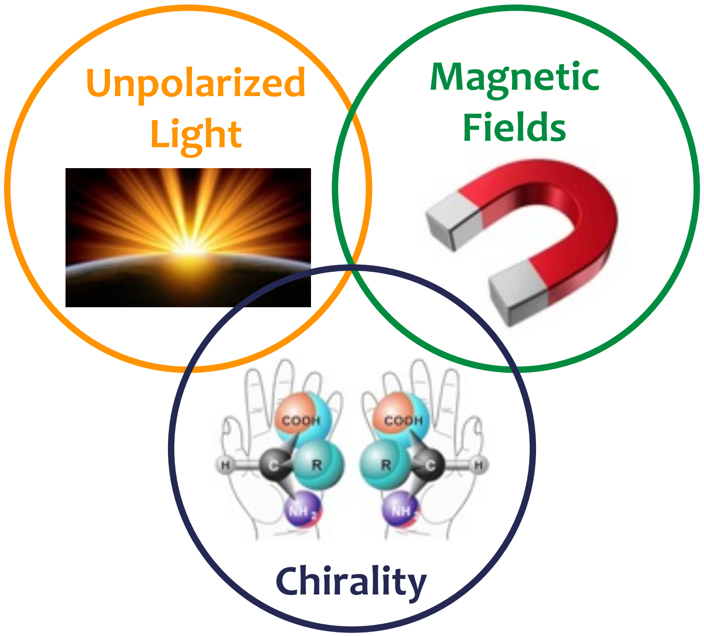
True Chiral Influence on Chiral Systems

Breaking both time-reversal and mirror symmetry leads to **Magneto-Chiral Anisotropy**

L. D. Barron, *Chem. Soc. Rev.* **1986**,15, 189

Light-Matter Interaction of Chiral Magnetized Systems

Magneto-Chiral Anisotropy: Magnetic Chiral Dichroism (MChD)

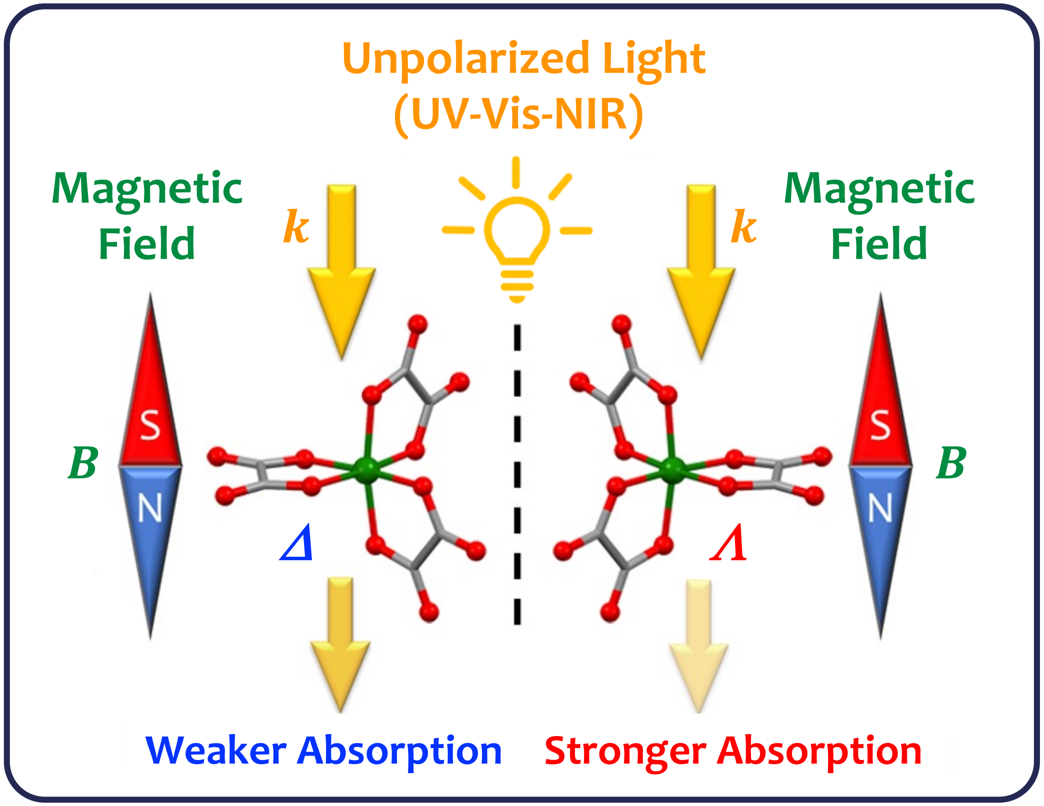


$$\varepsilon(\lambda, \boldsymbol{k}, \boldsymbol{B}) = \varepsilon_0(\lambda) \pm \alpha^{d/l}(\lambda)\boldsymbol{k} \pm \beta(\lambda)\boldsymbol{B} + \gamma^{d/l}(\lambda)\boldsymbol{k} \cdot \boldsymbol{B}$$

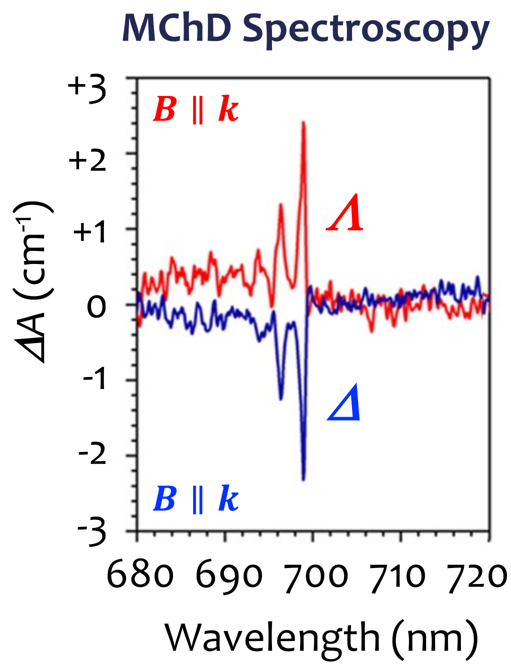
L. D. Barron & J. Vrbancich *Molecular Physics* **1984**,51, 715

Magneto-Chiral Dichroism (MChD)

The Light Absorption of Chiral Systems in Magnetic Fields is enantioselective



$$A = A_0 + \Delta A^{\Delta/\Lambda}$$



$$\Delta A^{\Delta/\Lambda} \propto \boldsymbol{M}(T, \boldsymbol{B})$$

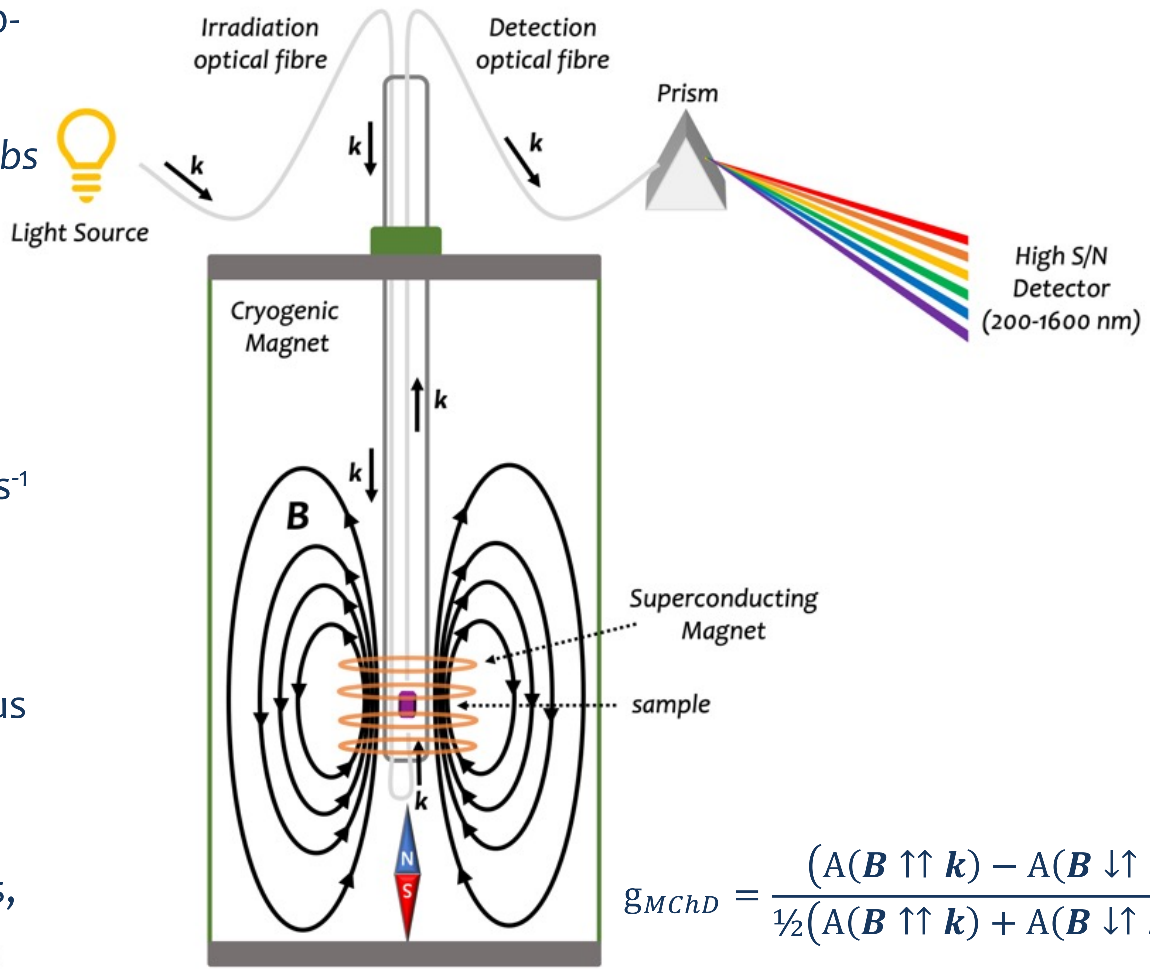
G. Rikken and E. Raupach, *Nature* **1997**, *390*, 493

Magneto-Chiral Dichroism (MChD)

A phenomenon difficult to detect:

Experimental setup available at the LNCMI

- ✓ **Spectral range:** UV-Vis-NIR (260-1600 nm)
- ✓ **Spectral detection:** *Abs* and *ΔAbs*
- ✓ ***T* range:** 290 K to 2.2 K
- ✓ ***B* range:** up to ±6 T (…10 T)
- ✓ ***B* frequency:** 0.04 to 1.5 Hz
- ✓ ***B* sweeping rate:** 800-3200 Oe s^{-1}
- ✓ ***B* profiles:** triangular, square, sinusoidal
- ✓ **Detection method:** Synchronous spectral detection during magnetic field sweep
- ✓ **Samples:** single crystals, pellets, drop casted samples, thin films

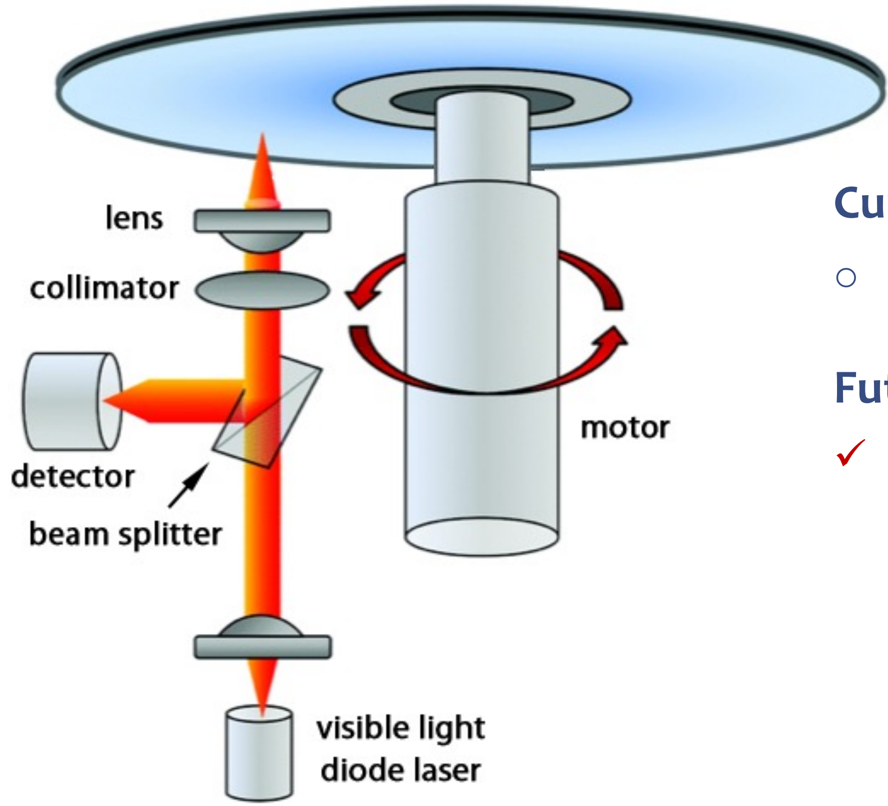


$$g_{MChD} = \frac{(A(\boldsymbol{B} \uparrow\uparrow \boldsymbol{k}) - A(\boldsymbol{B} \downarrow\uparrow \boldsymbol{k}))}{\frac{1}{2}(A(\boldsymbol{B} \uparrow\uparrow \boldsymbol{k}) + A(\boldsymbol{B} \downarrow\uparrow \boldsymbol{k}))\, \boldsymbol{B}}$$

Magneto-Chiral Dichroism

Potential Technological Application:

Optical read-out of magnetic data



Current Technology

- Circularly polarized light

Future Technology

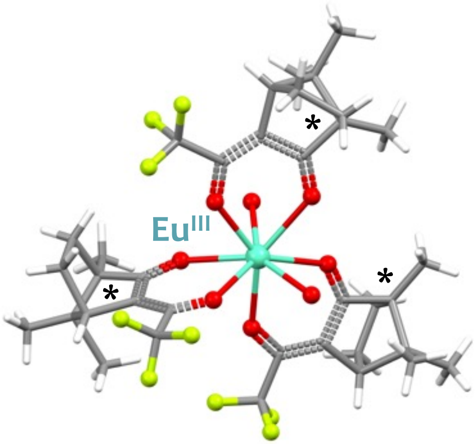
✓ **Unpolarized light**

Simpler device
No polarization
No PEM
Optical fibers

Nature Physics **2015**, *11*, 7

MChD in Chiral Molecular Systems

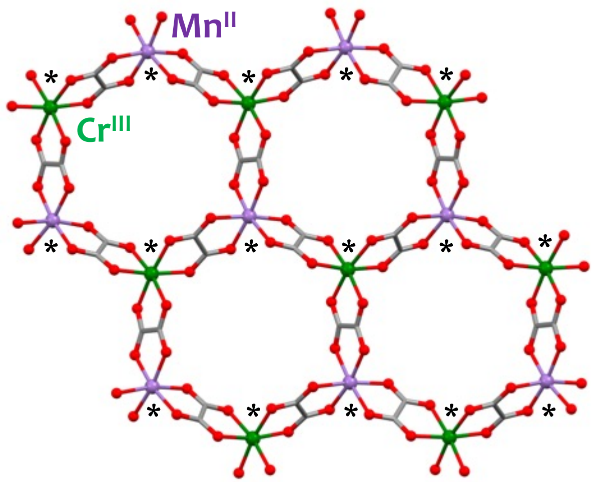
Chiral Ln Complex



$[Eu^{III}(d/l\text{-}tfc)_3]$

G. Rikken & E. Raupach
Nature **1997**

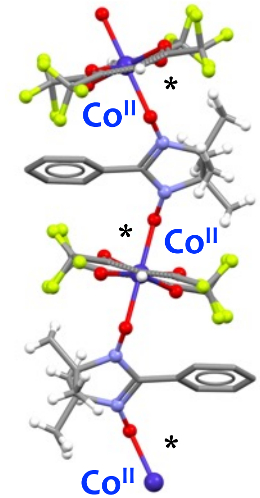
Chiral Molecular Ferromagnet



$[(\Delta/\Lambda)\text{-}Mn^{II}(\Lambda/\Delta)\text{-}Cr^{III}(C_2O_4)_3]^-$

C. Train, G. Rikken *et al.*
Nature Materials **2008**

Chiral Helical Chains



$[Co^{II}(hfac)_2NITPhOMe]$

R. Sessoli, A. Rogalev *et al.*
Nature Physics **2015**

- **Observed only in few systems**
- **Lack of systematic investigations**

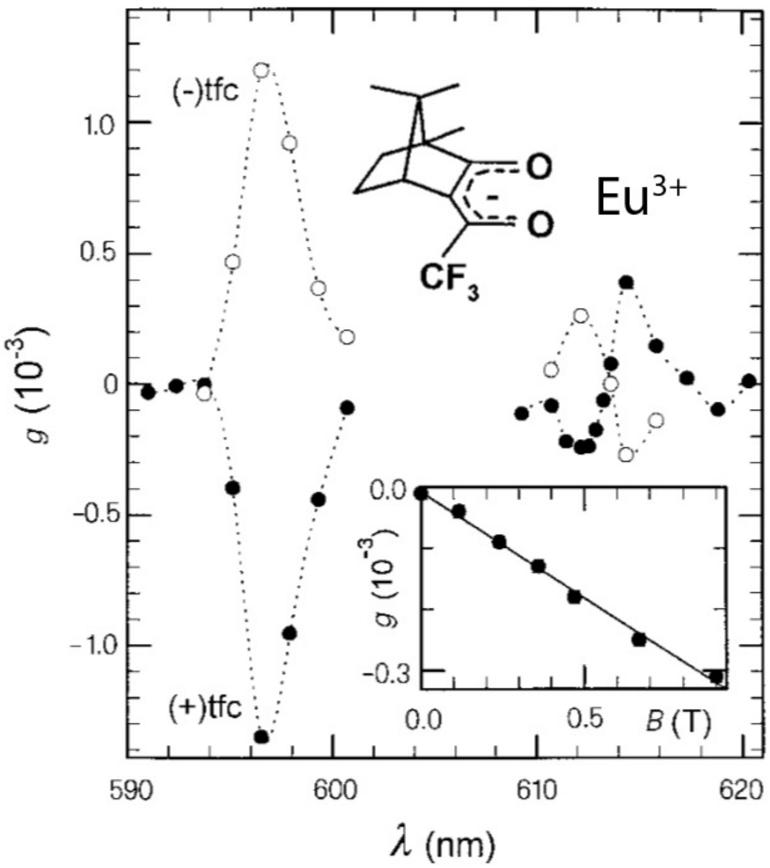
M. Atzori *et al.*, *Chem.–Eur. J.* **2020**, 26, 9784-9791

MChD in Chiral Molecular Systems

MChD probed by light emission: Luminescence of a chiral Ln complex

- **First experimental evidence of MChD**
- A chiral Eu^{III} complex with chiral ligands selected from the chiral pool
- $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions probed

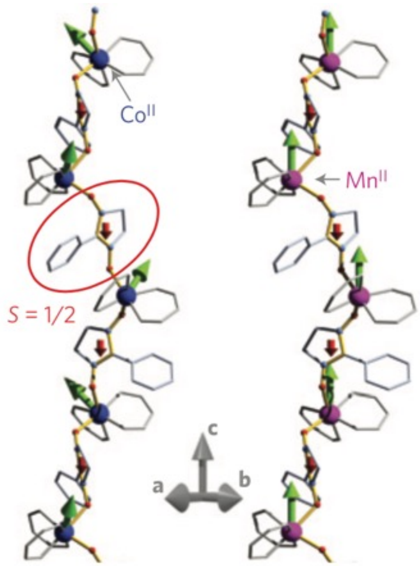
$$g_{MChD} = \frac{\left(I(\boldsymbol{B} \uparrow\uparrow \boldsymbol{k}) - I(\boldsymbol{B} \downarrow\uparrow \boldsymbol{k})\right)}{½\left(I(\boldsymbol{B} \uparrow\uparrow \boldsymbol{k}) + I(\boldsymbol{B} \downarrow\uparrow \boldsymbol{k})\right) \boldsymbol{B}}$$



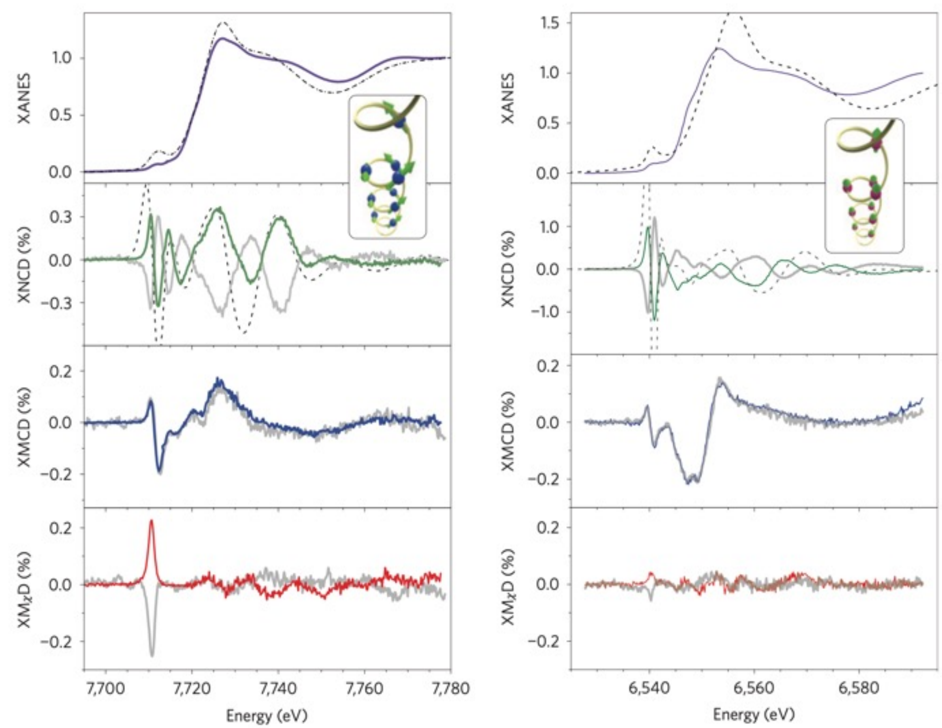
G. Rikken & E. Raupach *Nature* **1997**, *390*, 493

MChD in Chiral Molecular Systems

MChD probed by X-ray absorption: Helical Co^{II}-radical Single-Chain Magnet



- ✓ **Metal-radical 1D compounds obtained by spontaneous resolution**



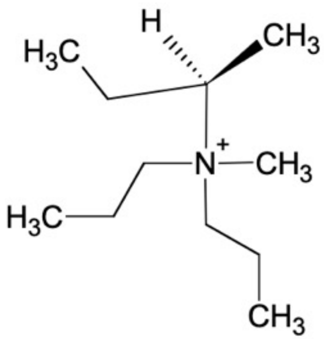
- ✓ **No signal** for the **Mn(II)** derivative
- ✓ **Strong signal** for the **Co(II)** derivative
- ✓ Influence of the orbital moment on the intensity of MChD

R. Sessoli *et al.*, *Nature Phys.* **2015,** *11*, 69

MChD in Chiral Molecular Systems

MChD probed by Visible light absorption:

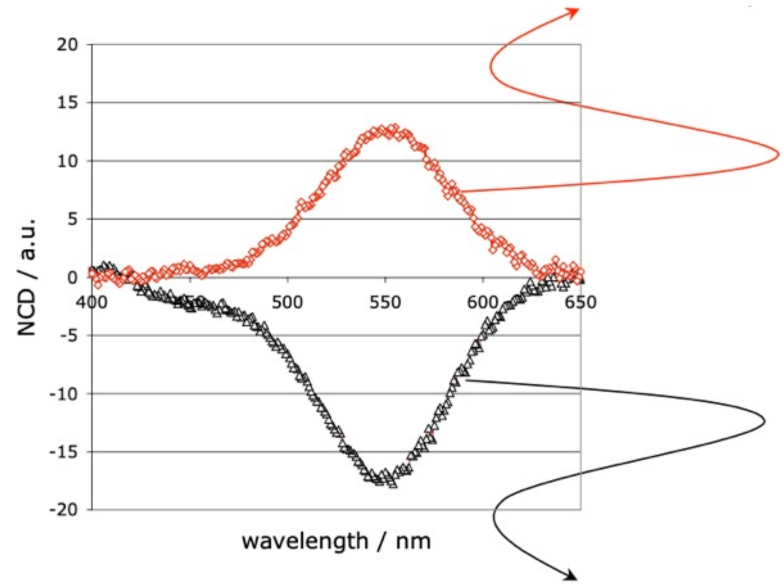
Enantiopure Chiral Ferromagnet obtained by enantioselective self-assembly



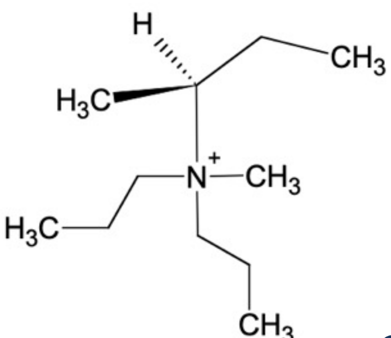
$NMePr_2$(*R*)-*sec*-Bu^+

$(NH_4)_3[(rac)\text{-}Cr^{III}(C_2O_4)_3]$ → Mn^{II}

$[NMePr_2(R)\text{-}sec\text{-}Bu][(\Delta)\text{-}\mathbf{Mn^{II}}(\Lambda)\text{-}\mathbf{Cr^{III}}(C_2O_4)_3]$



$NMePr_2$(*S*)-*sec*-Bu^+



$(NH_4)_3[(rac)\text{-}Cr^{III}(C_2O_4)_3]$ → Mn^{II}

$[NMePr_2(S)\text{-}sec\text{-}Bu][(\Lambda)\text{-}\mathbf{Mn^{II}}(\Delta)\text{-}\mathbf{Cr^{III}}(C_2O_4)_3]$

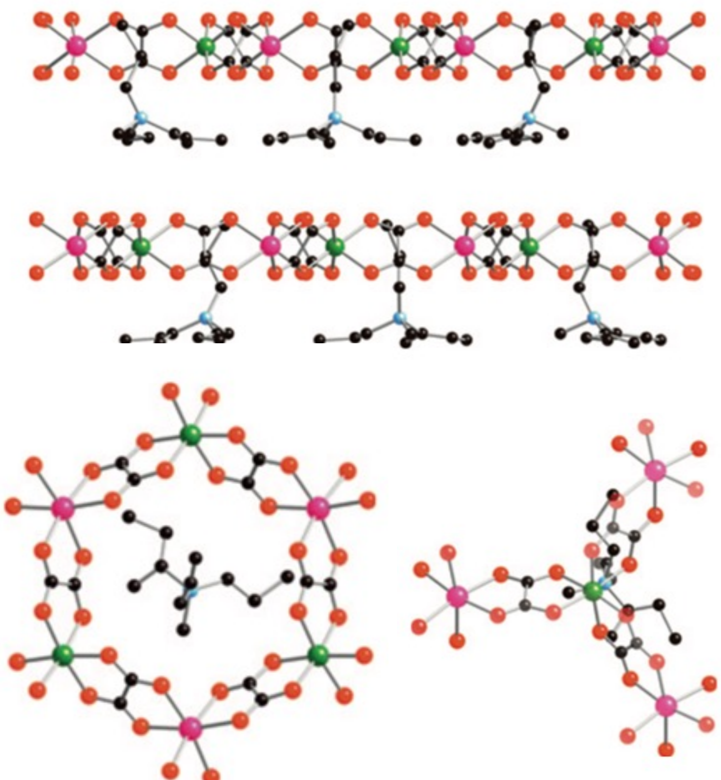
Control of chirality by the template cation

C. Train *et al.*, *Nature Mater.* **2008**, 7, 729

MChD in Chiral Molecular Systems

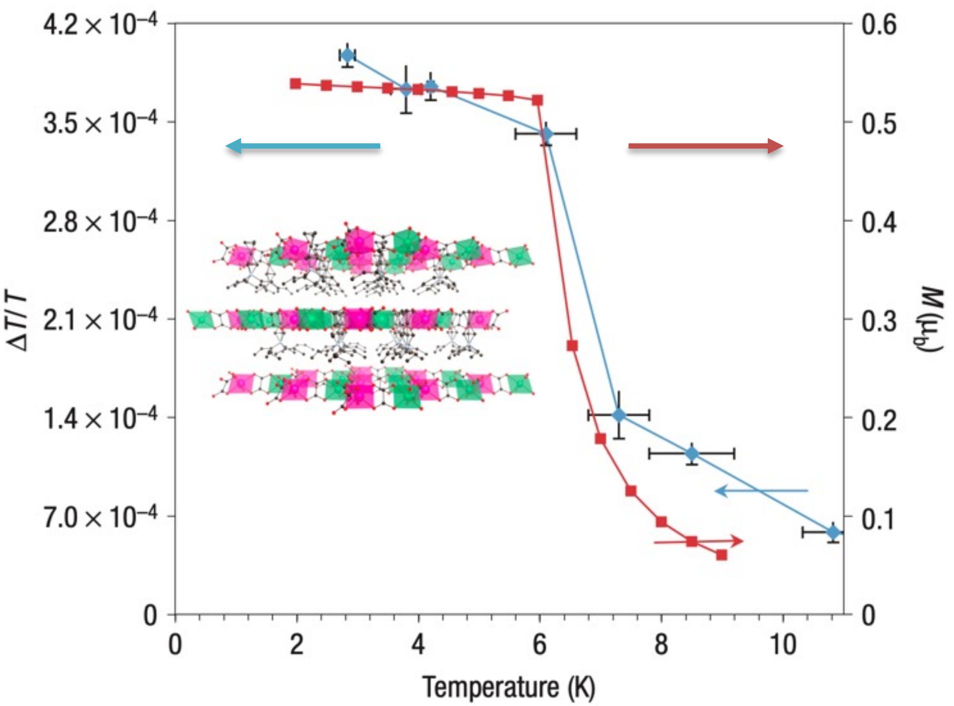
MChD probed by Visible light absorption:

Enantiopure Chiral Ferromagnet obtained by enantioselective self-assembly



Space Group $P6_3$

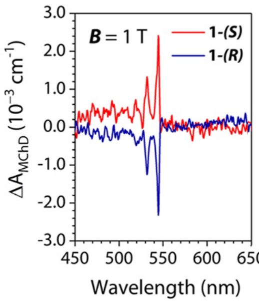
$[(\Delta)\text{-}\mathbf{Mn^{II}}(\Lambda)\text{-}\mathbf{Cr^{III}}(C_2O_4)_3]^-$ or $[(\Lambda)\text{-}\mathbf{Mn^{II}}(\Delta)\text{-}\mathbf{Cr^{III}}(C_2O_4)_3]^-$

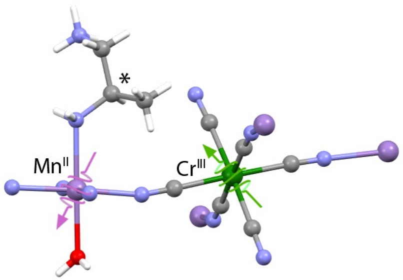


The intensity of MChD increases by a factor of 6 passing from the paramagnetic to the ferromagnetic phase

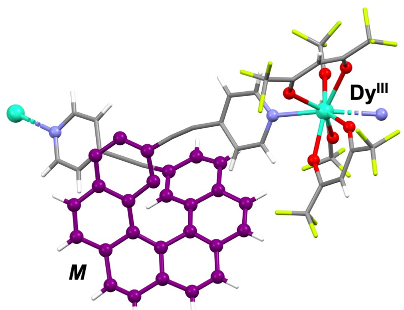
C. Train *et al.*, *Nature Mater.* **2008**, 7, 729

My contribution to this Research Field

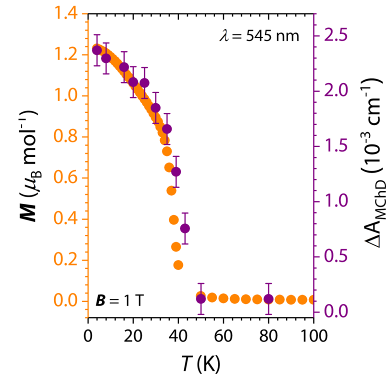




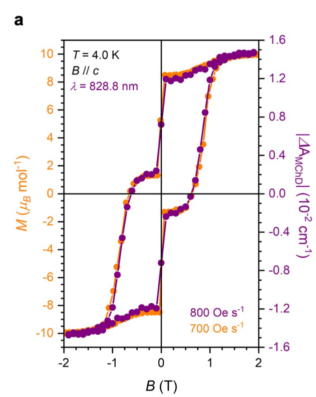
1. **Understand the microscopic physico-chemical parameters governing MChD**



2. **Enhance the strength of MChD** by chemical design



3. **Increase the temperature** at which this phenomenon is observed



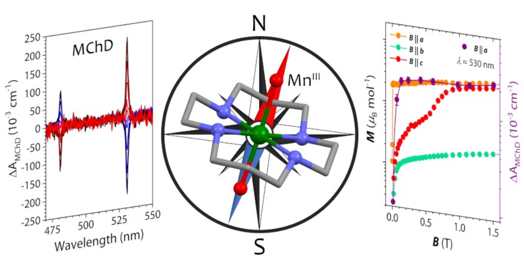
4. Prove that **MChD** is a **technological relevant optical phenomenon**

Overview of Investigated Systems

MChD investigation in:

Transition Metal Complexes

- ✓ *J. Am. Chem. Soc.* **2019**, 141, 20022
- ✓ *J. Am. Chem. Soc.* **2020**, 142, 13908
- ✓ *Sci. Adv.* **2021**, 7, eabg2859
- ✓ *J. Am. Chem. Soc.* **2022**, 144, 8837
- ✓ *J. Mater. Chem. C*, **2022**, 10, 13939

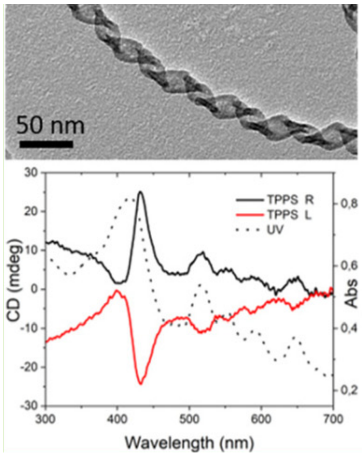


Lanthanides Complexes

- ✓ *J. Am. Chem. Soc.* **2021**, 143, 2671
- ✓ *J. Am. Chem. Soc.* **2022**, 144, 8837
- ✓ *Angew. Chem. Int. Ed.* **2022**, 62, e202215558
- ✓ *Inorg. Chem.* **2023**, 62, 17583
- ✓ *J. Am. Chem. Soc.* **2024**, 146, 16389
- ✓ *J. Am. Chem. Soc.* **2024**, 146, 23624
- ✓ *Angew. Chem. Int. Ed.* **2024**, 63 e202412521

Chiral Nanostructures

- ✓ *A. Phys. Lett.* **2021**, 118, 251108
- ✓ *Nanoscale* **2023**, 15, 12095



Review Articles

- ✓ *Chem. Eur. J.* **2020**, 26, 9784
- ✓ *Chirality* **2021**, 33, 844
- ✓ *Inorg. Chem. Front.* **2024**, 11, 1313

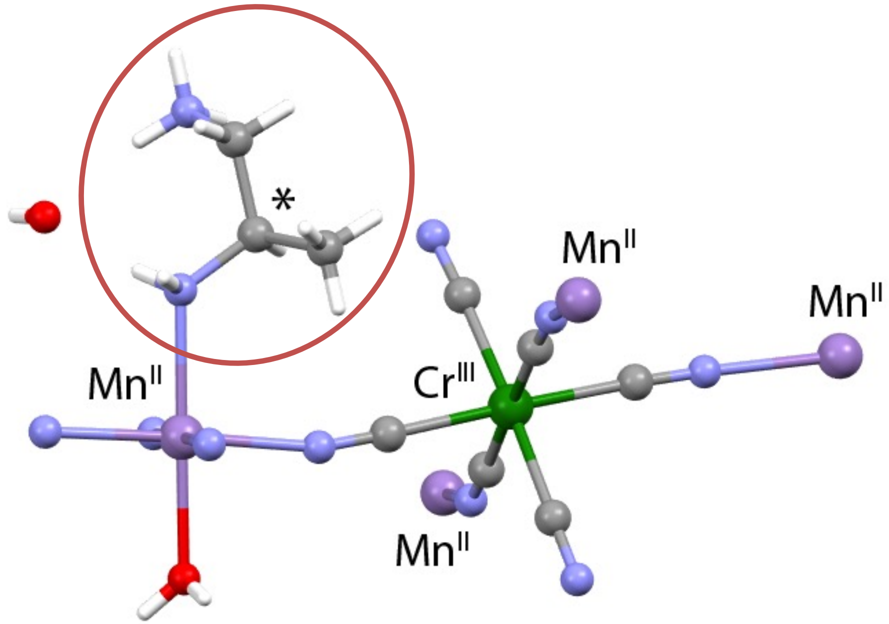
Molecular Chemistry | *Reviews Showcase* |

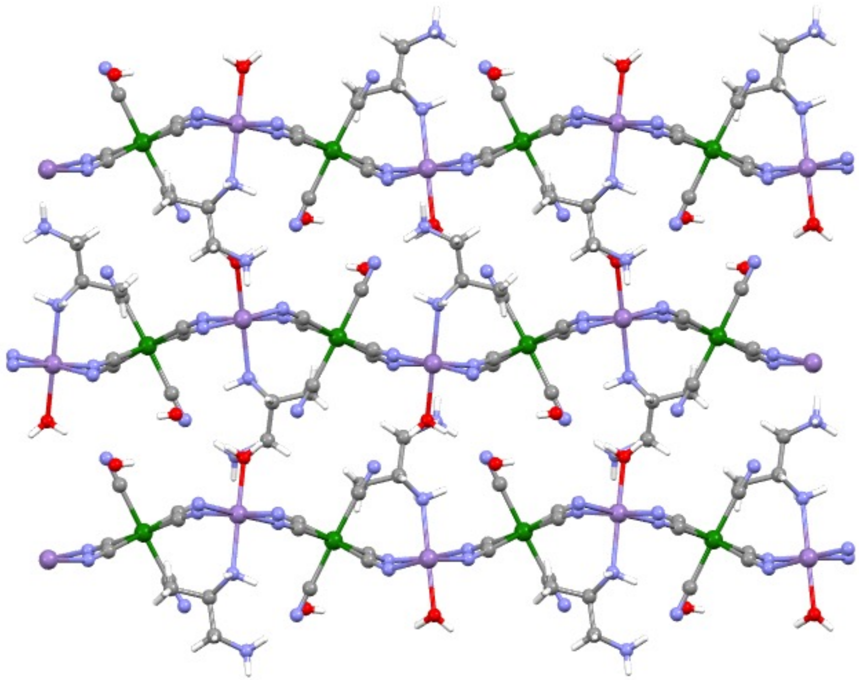
Magneto-Chiral Dichroism: A Playground for Molecular Chemists

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

1. MChD in heterometallic Chiral Magnets

Motivation: Increase MChD viable temperature by chemical design





Chiral Prussian Blue Analogue [**Cr^{III}**$(CN)_6$][**Mn^{II}**((*X*)-pnH)(H_2O)]·H_2O

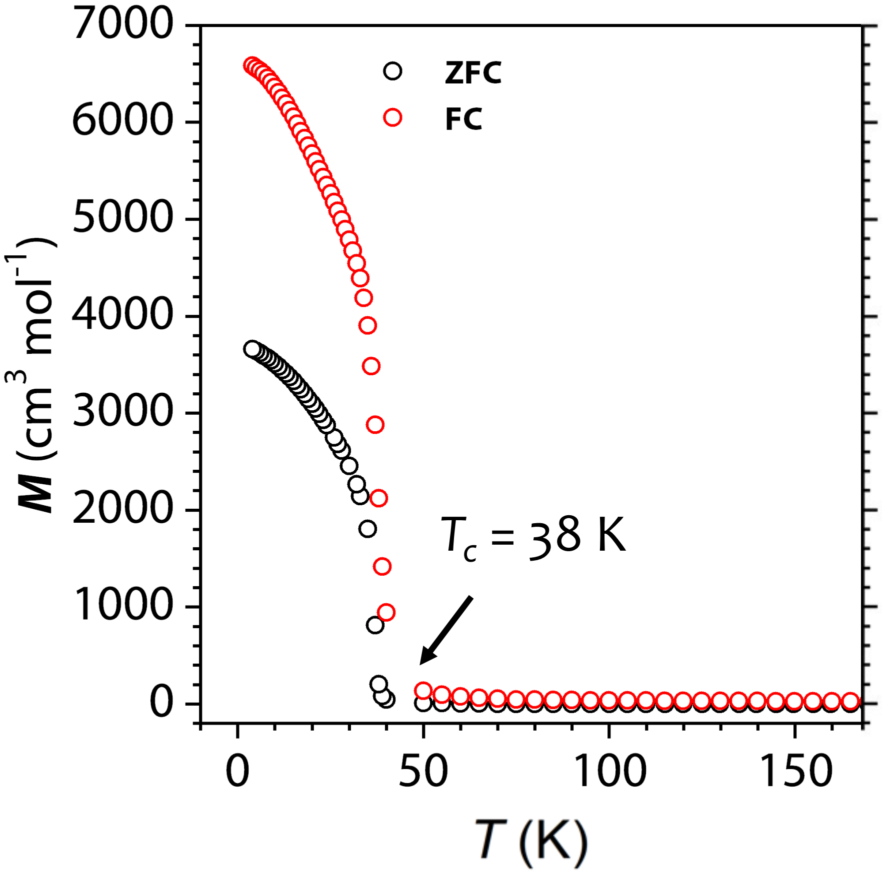
(X = *S*, *R*; pnH = 1,2-diaminopropane **as chiral coligand**)

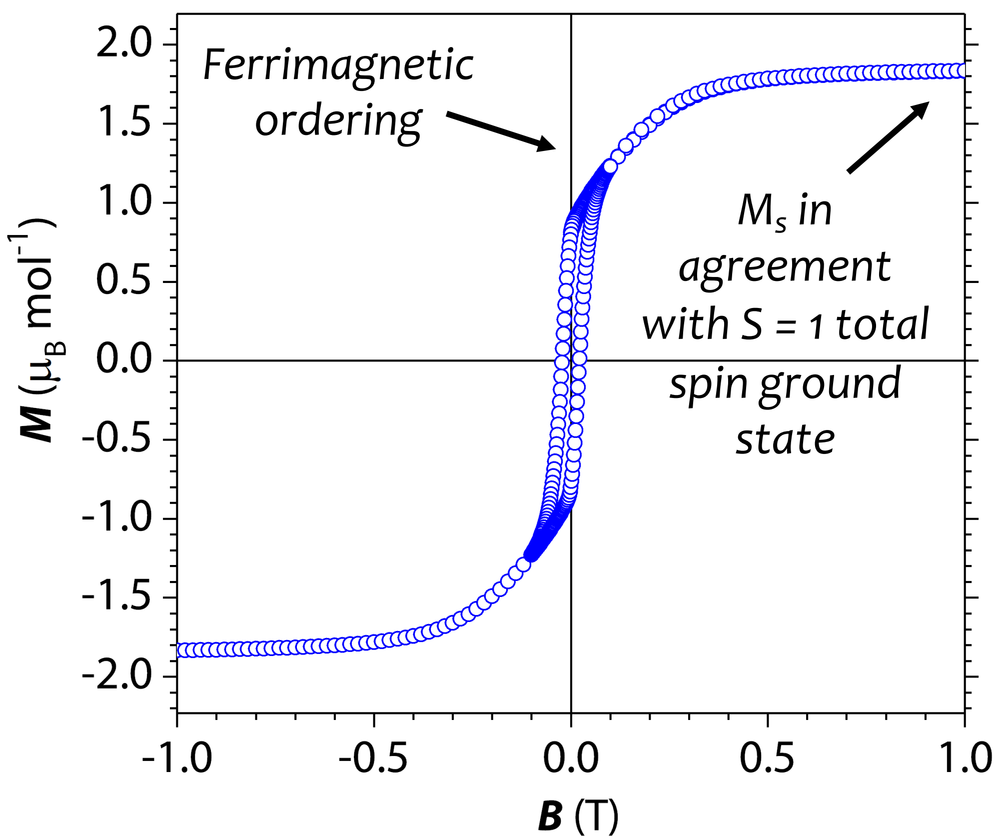
2D-layered structure

K. Inoue *et al. Angew. Chem. Int. Ed.* **2003**, 42, 4810

1. MChD in heterometallic Chiral Magnets

Magnetic Properties



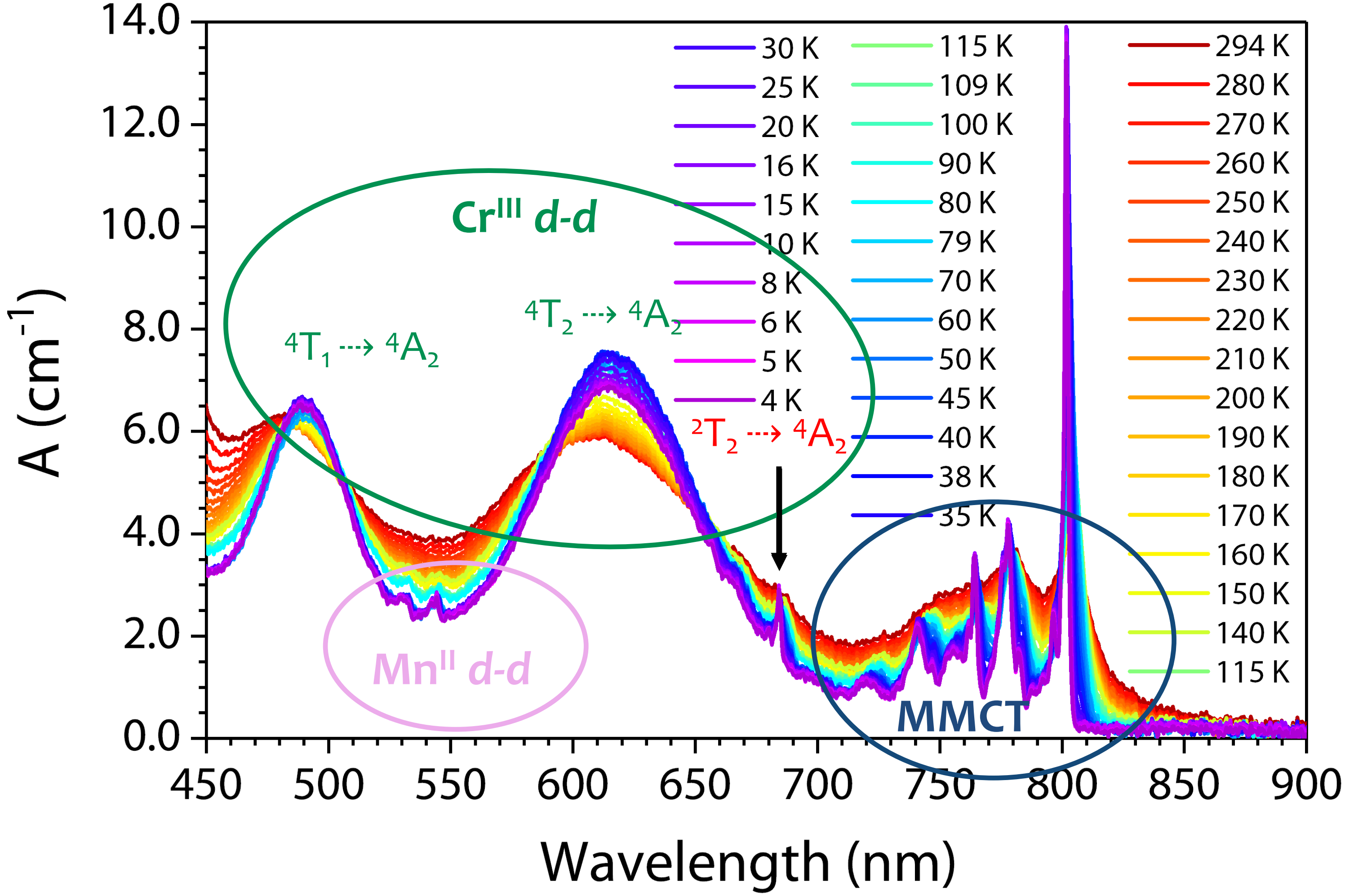


Molecular ferrimagnet with a relatively high ordering temperature: 38 K

M. Atzori *et al. J. Am. Chem. Soc.* **2019**, *141*, 20022

1. MChD in heterometallic Chiral Magnets

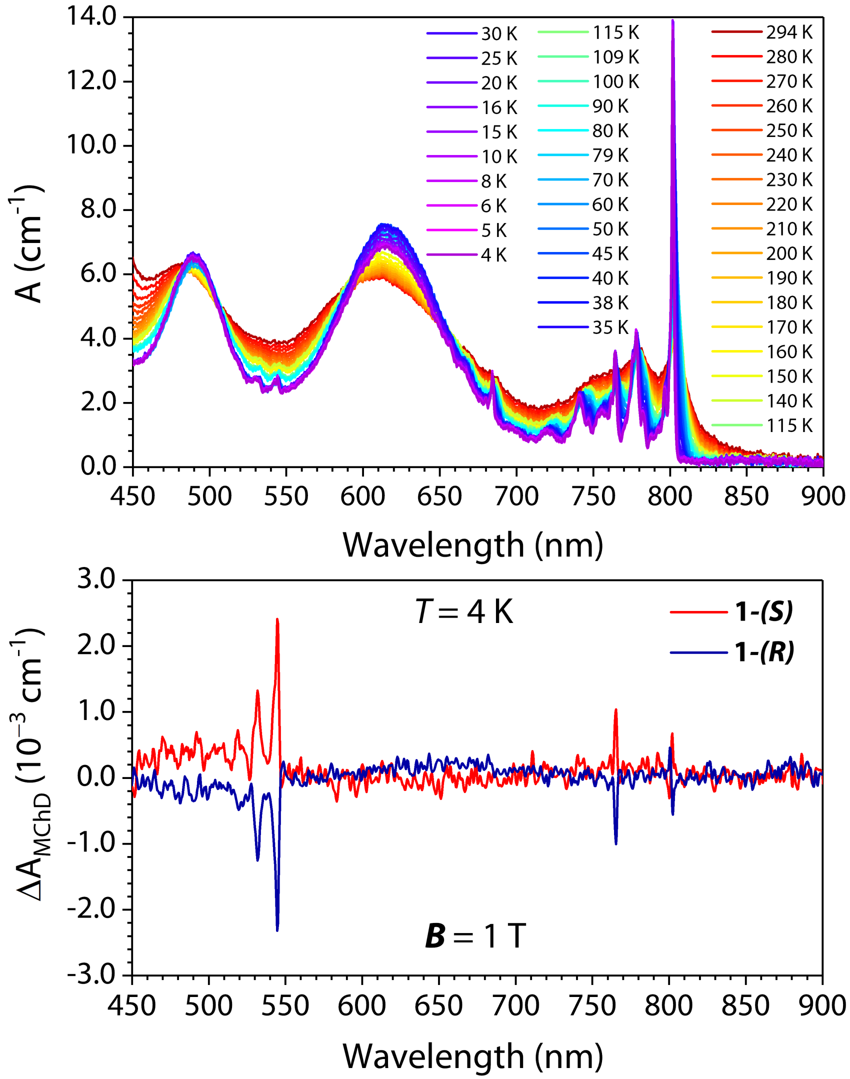
Temperature dependence of absorption in the Visible



M. Atzori *et al. J. Am. Chem. Soc.* **2019**, *141*, 20022

1. MChD in heterometallic Chiral Magnets

Magneto-Chiral Optical Response: MChD

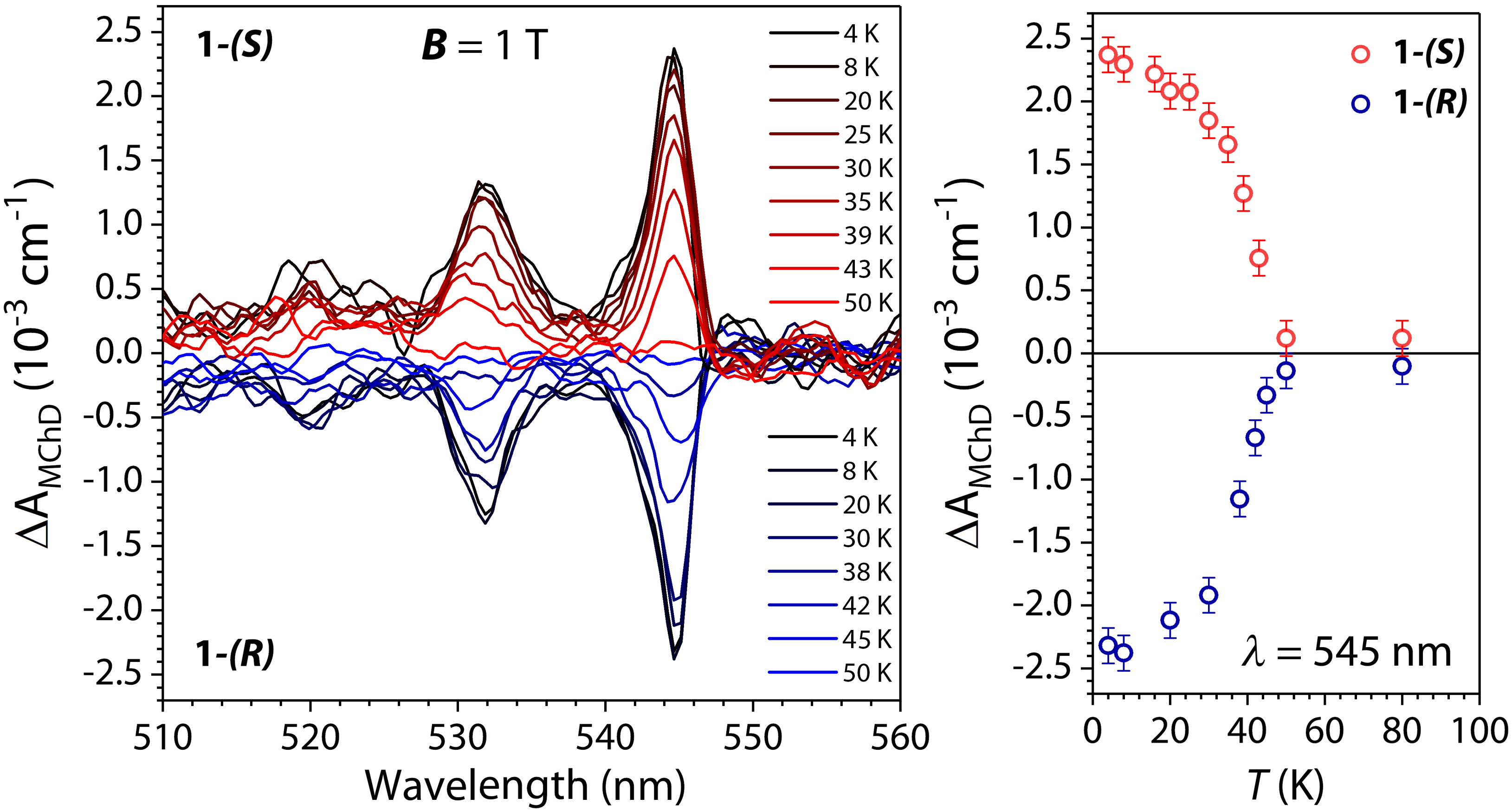


- ✓ MChD is observed despite the **second coordination sphere chiral features of the magnetic centers**
- ✓ **Mirror images of MChD** observed for the two enantiomers
- ✓ **MChD signals arises from Mn^{II}**, with a negligible orbital contribution to the magnetic moment but coordinated by the chiral ligand

M. Atzori *et al. J. Am. Chem. Soc.* **2019**, *141*, 20022

1. MChD in heterometallic Chiral Magnets

Temperature dependence of MChD signals

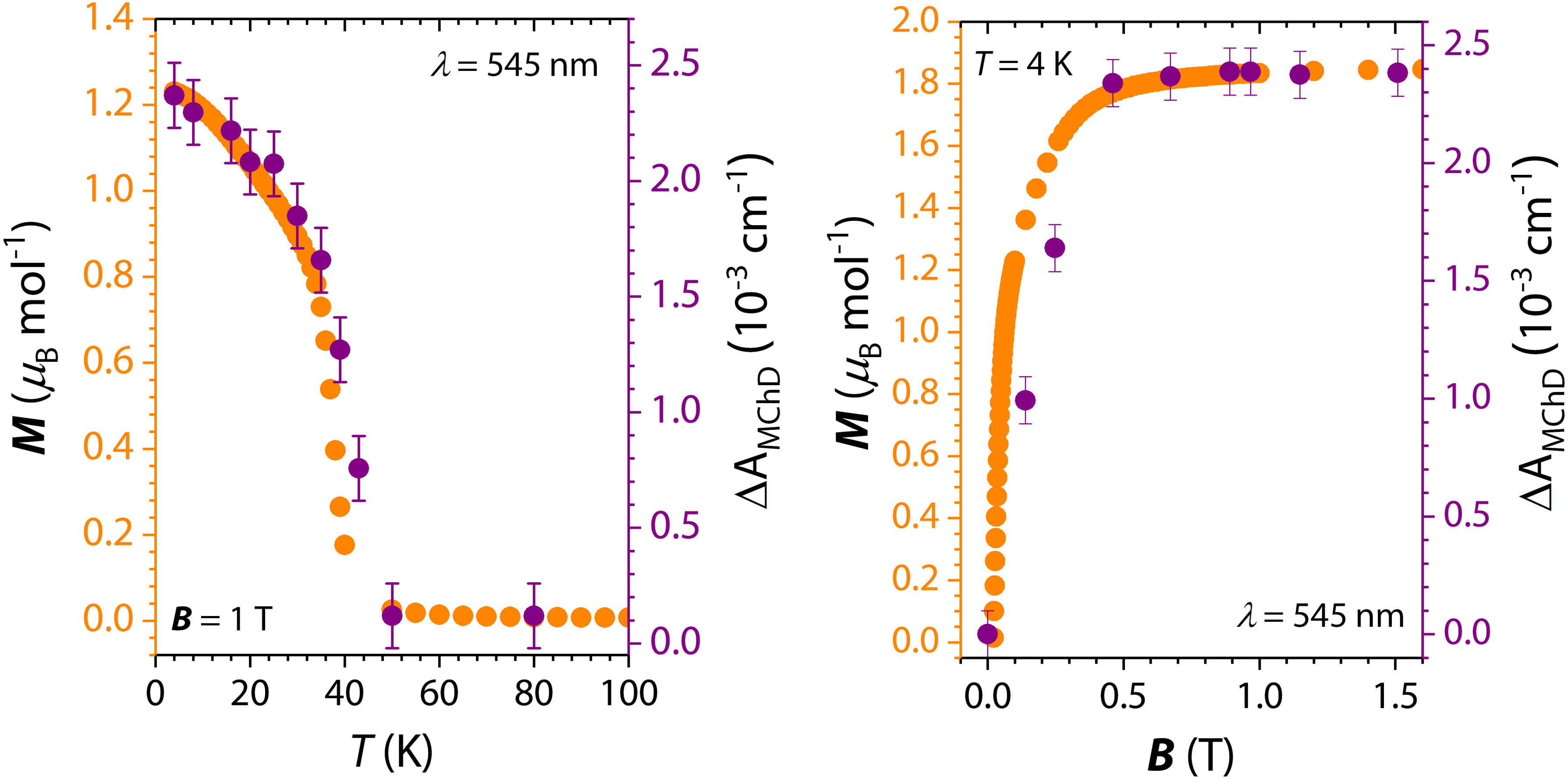


MChD persists up to 43 K

M. Atzori *et al. J. Am. Chem. Soc.* **2019**, *141*, 20022

1. MChD in heterometallic Chiral Magnets

Temperature and Field dependence of MChD and Magnetization

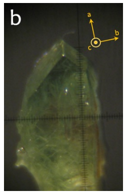


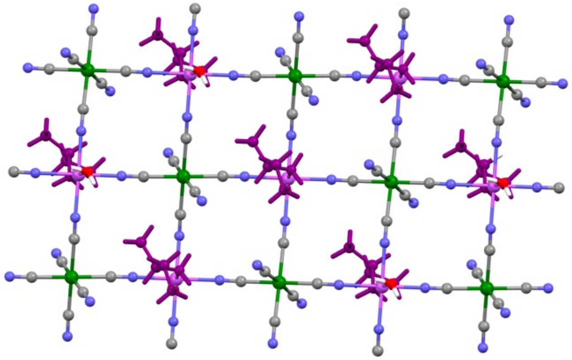
MChD signals accurately follow the magnetization as a function of *T* and *B*

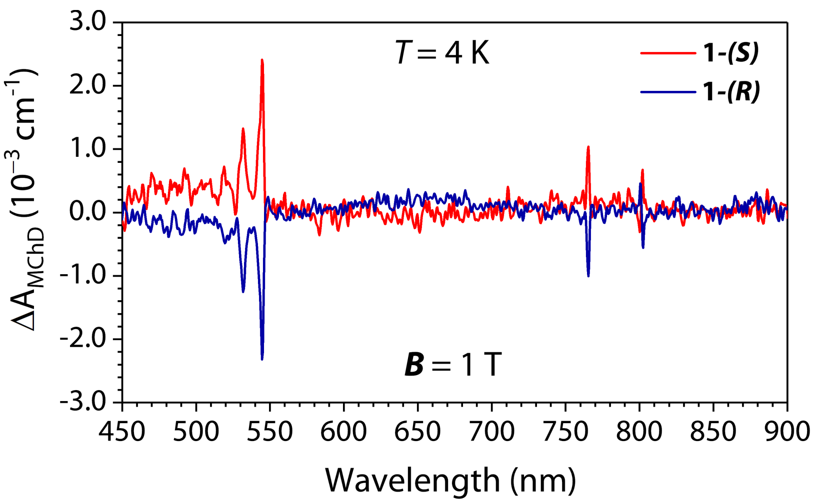
M. Atzori *et al. J. Am. Chem. Soc.* **2019**, *141*, 20022

1. MChD in heterometallic Chiral Magnets

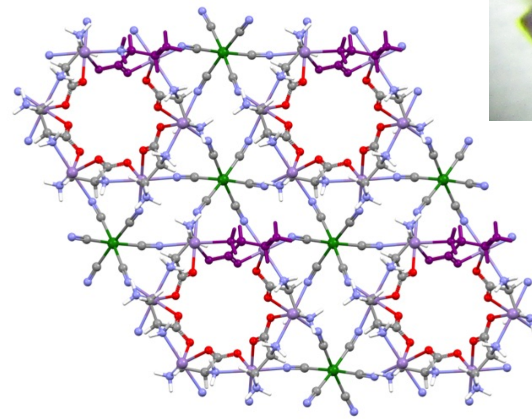
2D layered structures

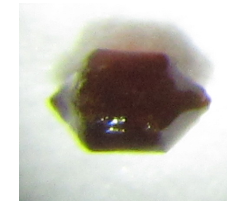


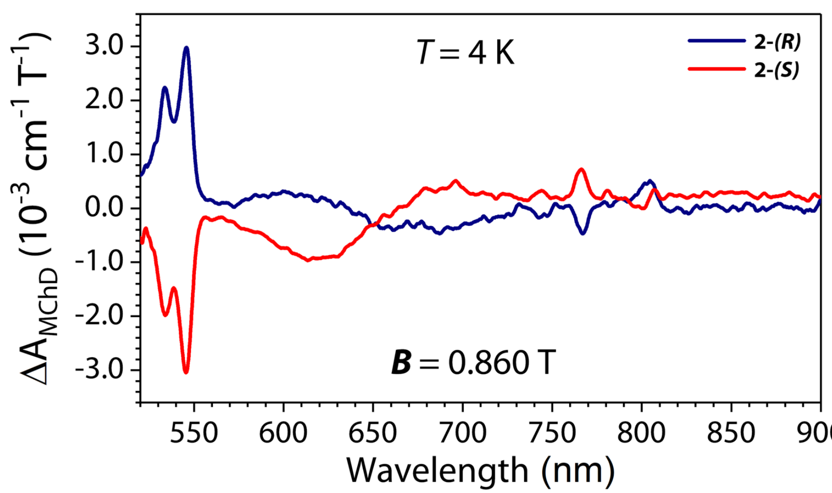




3D helical structures



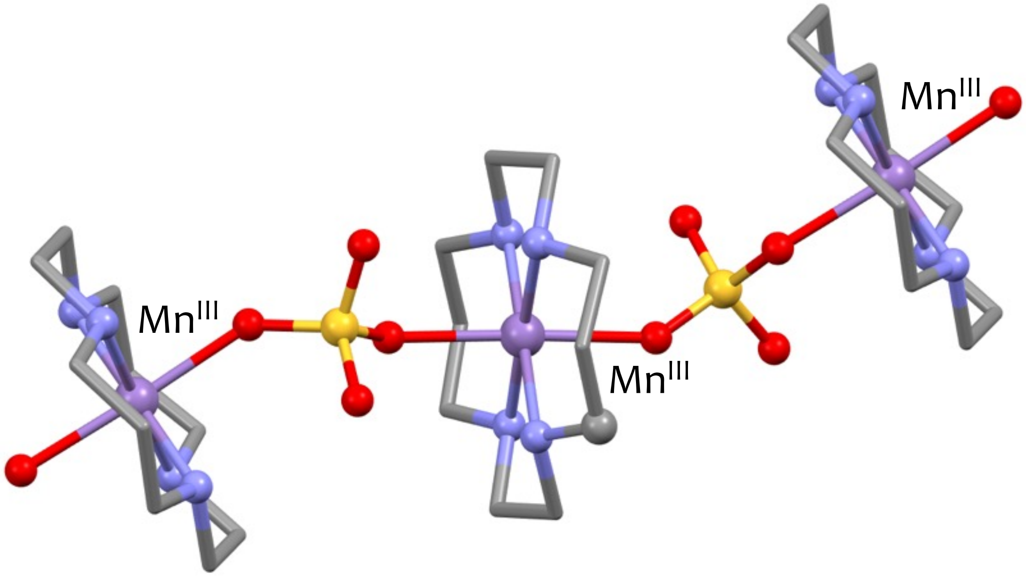


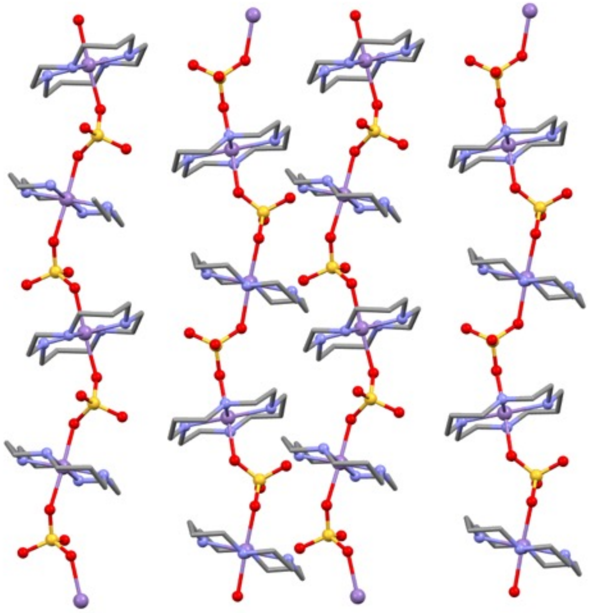


M. Atzori *et al. J. Mater. Chem. C* **2022**, *10*, 13939-13945

2. MChD in Chiral Supramolecular Chains

Motivation: Correlate MChD to Magnetic Anisotropy





[$\mathbf{Mn^{III}}$(cyclam)(SO_4)]$ClO_4 \cdot H_2O$

(cyclam = 1,4,8,11-tetraazacyclotetradecane)

Structure made of 1D chiral chains by spontaneous resolution

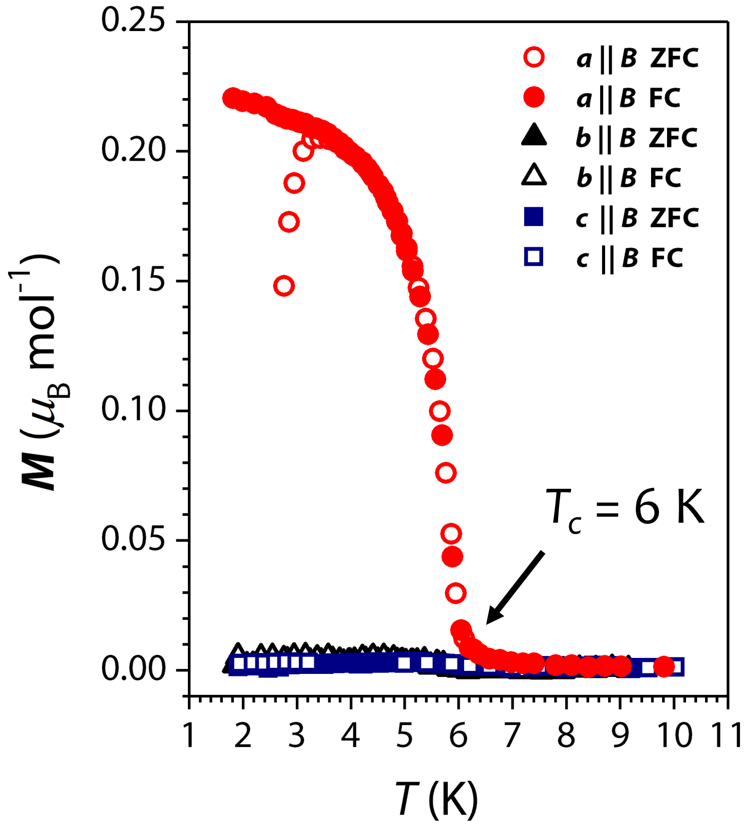
S. Mossin *et al. Dalton. Trans.*, **2004**, 632-639

With: R. Sessoli, F. Santanni, A. Caneschi (Florence – Italy)

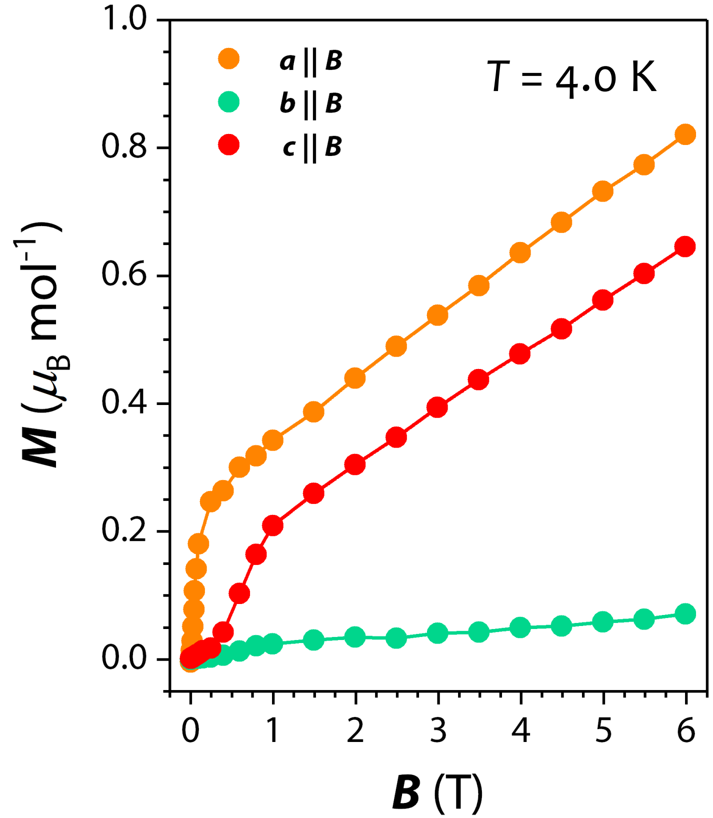
2. MChD in Chiral Supramolecular Chains

Magnetic Properties

T dependence of ***M***



B dependence of ***M***



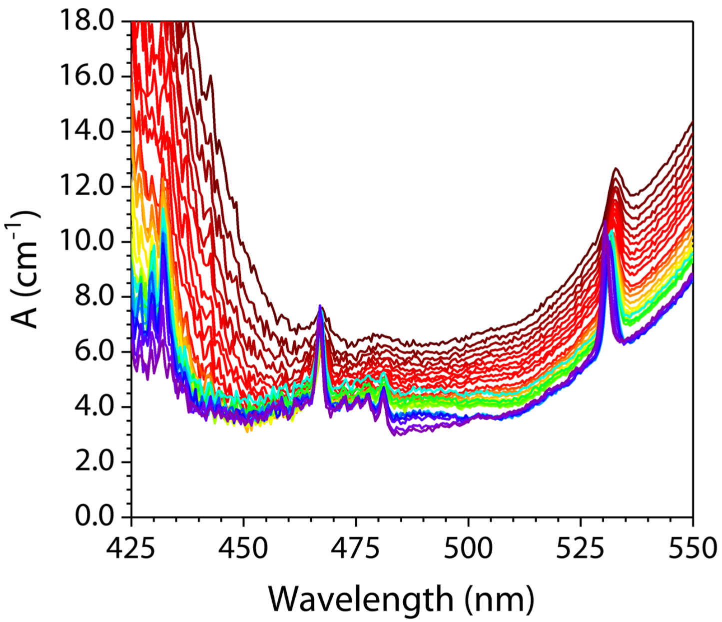
Magnetic behaviour of a canted antiferromagnet (weak ferromagnet)

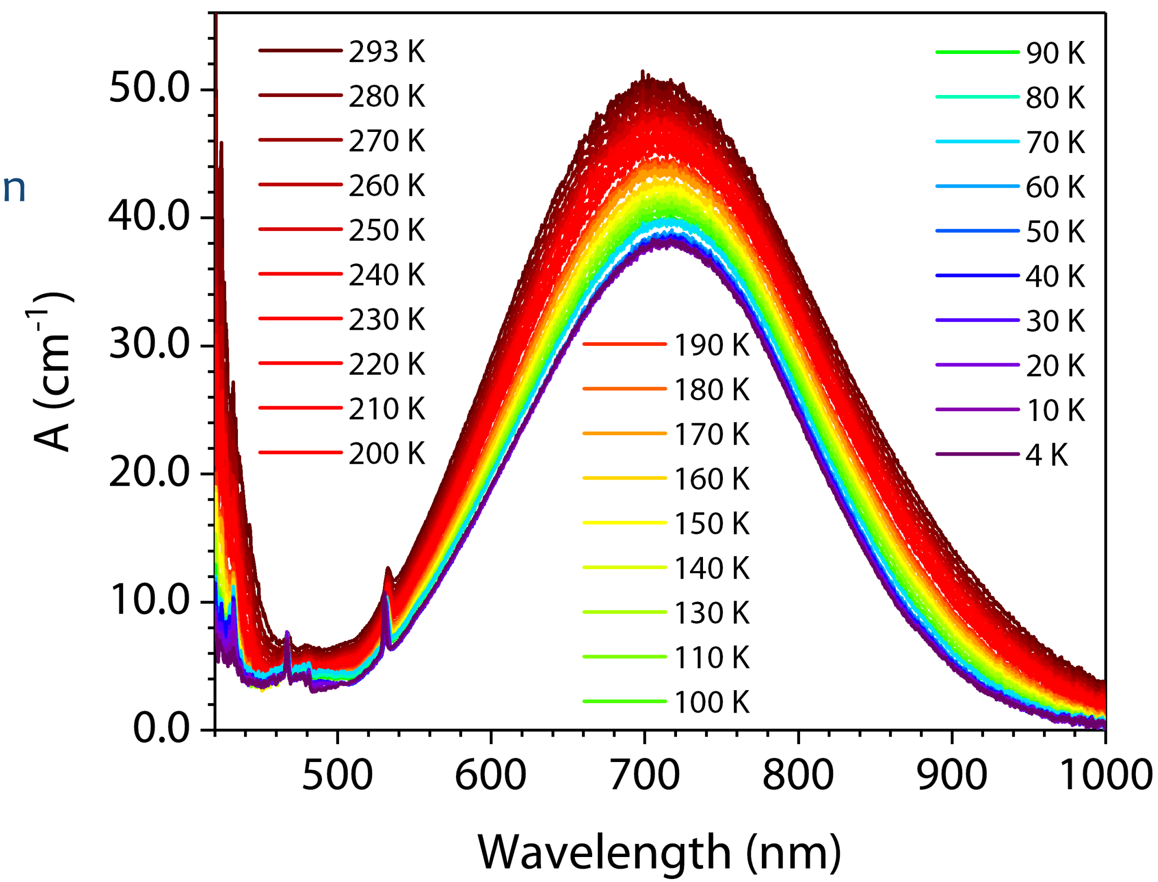
S. Mossin *et al. Dalton. Trans.*, **2004**, 632-639

2. MChD in Chiral Supramolecular Chains

Temperature dependence of absorption in the Visible

- ✓ **Single-crystal Visible light Absorption** down to 4 K
- ✓ Spin–allowed and spin–forbidden **electronic transitions of Mn^{III}** identified

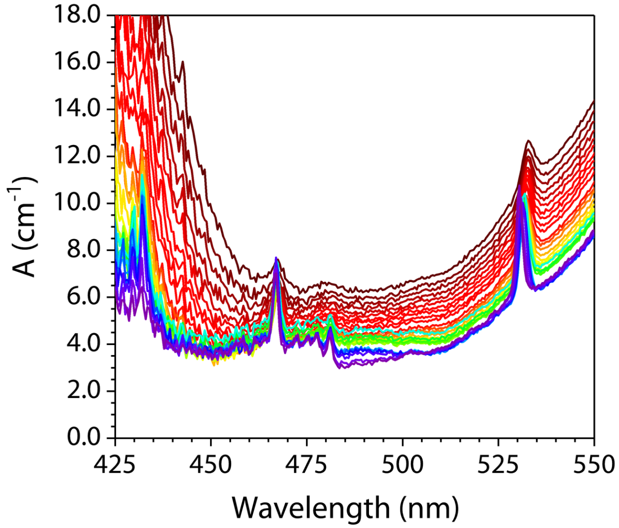


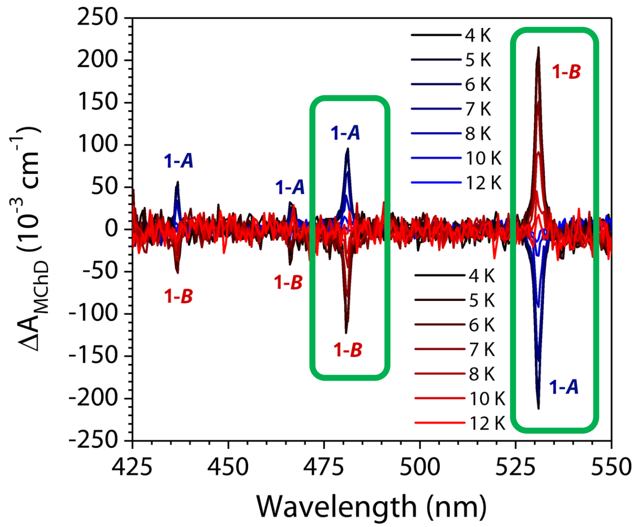


M. Atzori *et al. J. Am. Chem. Soc.* **2020**, *142*, 13908-13916

2. MChD in Chiral Supramolecular Chains

Magneto-Chiral Optical Response: MChD





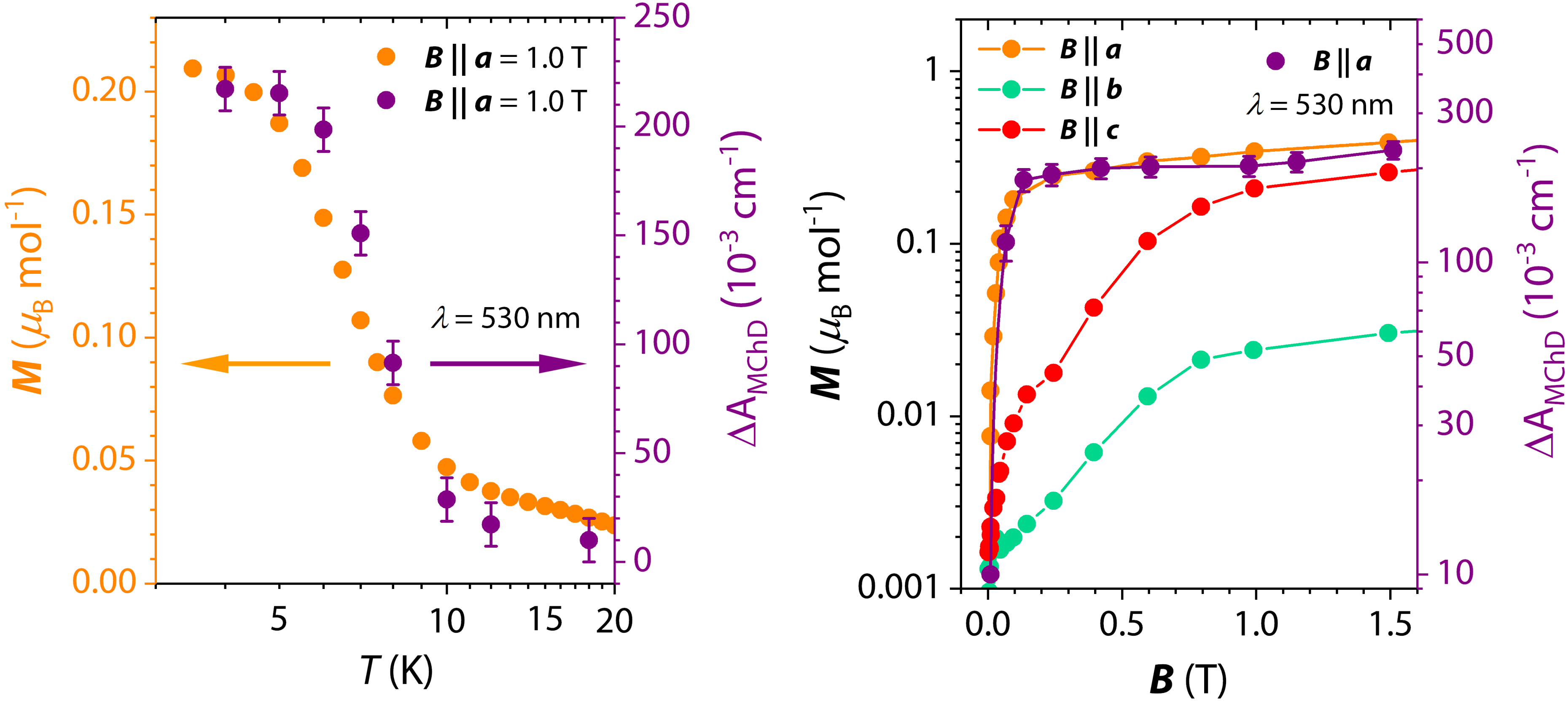
- ✓ Mirror MChD spectra observed for the two enantiomers
- ✓ MChD observed despite the second coordination sphere chiral features of the magnetic centers
- ✓ **Strong signals arises from the *d-d* transitions associated to spin-orbit character**

λ (nm)	*Electronic Transition*	$\lvert\Delta A_{MChD}\rvert$ (cm^{-1} T^{-1})	A (cm^{-1})	g_{MChD}	*SOC character*
432	$^5E_g \leftarrow {}^5B_{1g}$	0.06(1)	1.5(5)	**0.080(5)**	λ^2
467	$^3A_{2g} \leftarrow {}^5B_{1g}$	0.03(1)	3.6(5)	**0.017(5)**	**0**
481	$^3E_g \leftarrow {}^5B_{1g}$	0.09(1)	1.4(5)	**0.13(5)**	$4\lambda^2$
530	$^5B_{2g} \leftarrow {}^5B_{1g}$	0.21(1)	3.8(5)	**0.11(5)**	$4\lambda^2$
715	$^5A_{1g} \leftarrow {}^5B_{1g}$	0	38.0(5)	**0**	**0**

M. Atzori *et al.* *J. Am. Chem. Soc.* **2020**, *142*, 13908-13916

2. MChD in Chiral Supramolecular Chains

Temperature and Field dependence of MChD and Magnetization



MChD signals follow the *T* and *B* dependence of *M* and reproduce the strong magnetic anisotropy of the system

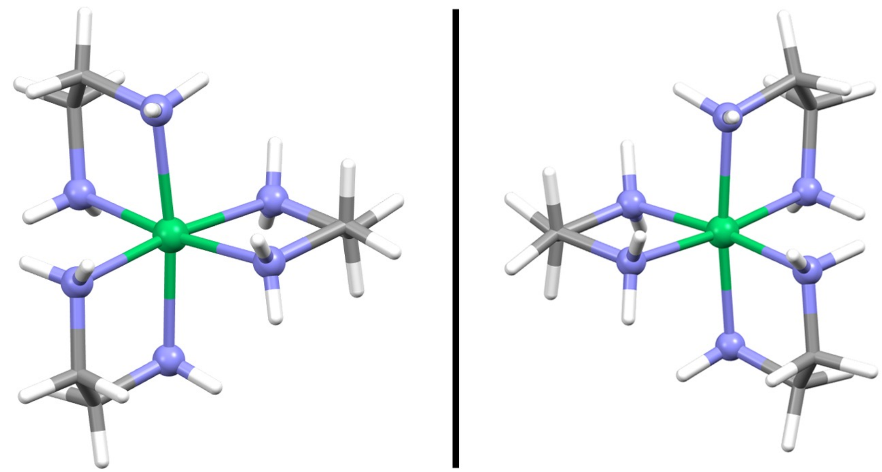
M. Atzori *et al. J. Am. Chem. Soc.* **2020**, *142*, 13908-13916

3. MChD in Enantiopure Magnetic Complexes

Motivation: Understand the microscopic parameters governing MChD

$[\mathbf{M}^{II}(en)_3](NO_3)_2$ (en = ethylenediamine, **M** = Ni^{II}, Co^{II})

- ✓ **Enantiopure Λ and Δ complexes** obtained by spontaneous resolution
- ✓ Large and **optical transparent** single crystals
- ✓ Isolated metal centers: **only M^{II} *d-d* transitions probed**
- ✓ Paramagnetic behavior
- ✓ **Intense NCD at the metal center**



$[(\Lambda)\text{-}M^{II}(en)_3]^{2+}$ $[(\Delta)\text{-}M^{II}(en)_3]^{2+}$

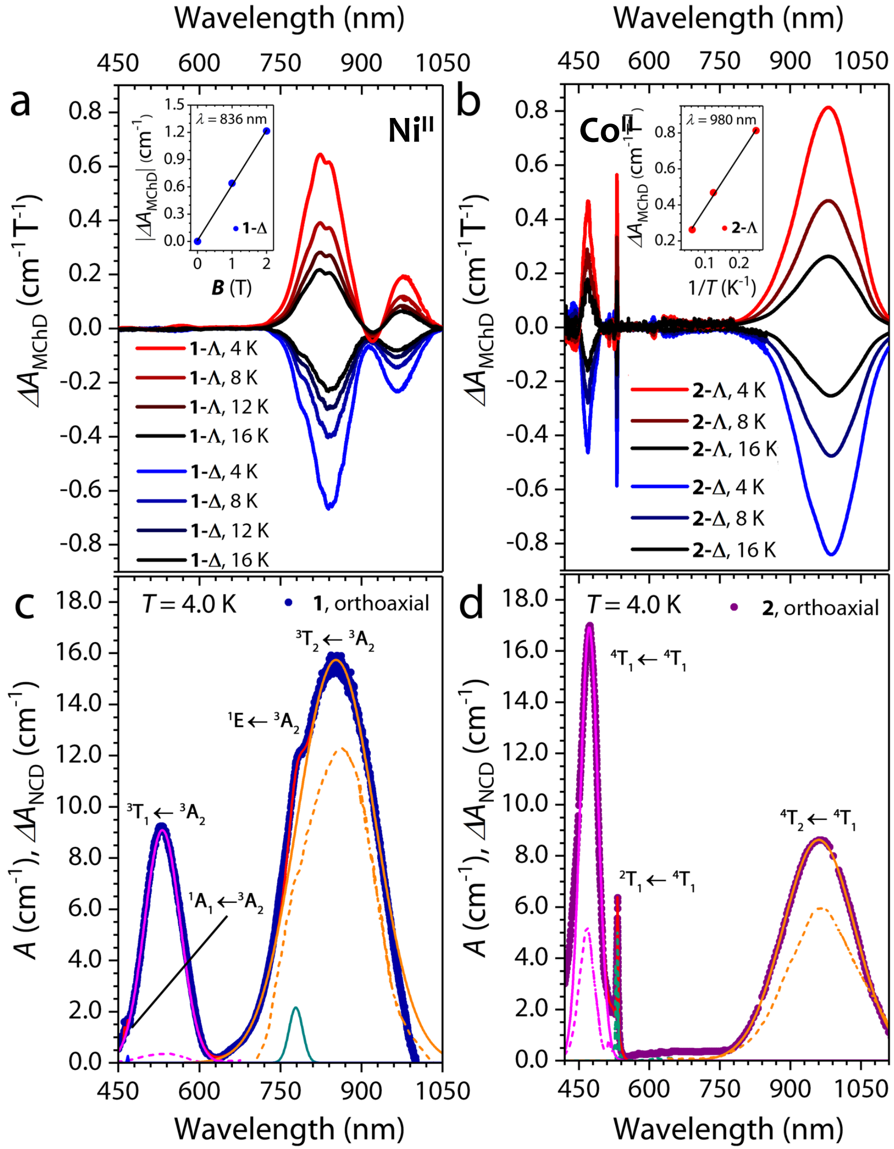
$[\mathbf{Ni}^{II}(en)_3](NO_3)_2$

With: E. Hillard, P. Rosa (ICMCB, Univ. Bordeaux)

M. Atzori *et al. Sci. Adv.* **2021**, 7, eabg2859

3. MChD in Enantiopure Magnetic Complexes

MChD data as a function of the temperature compared to optical absorption and Natural Circular Dichroism

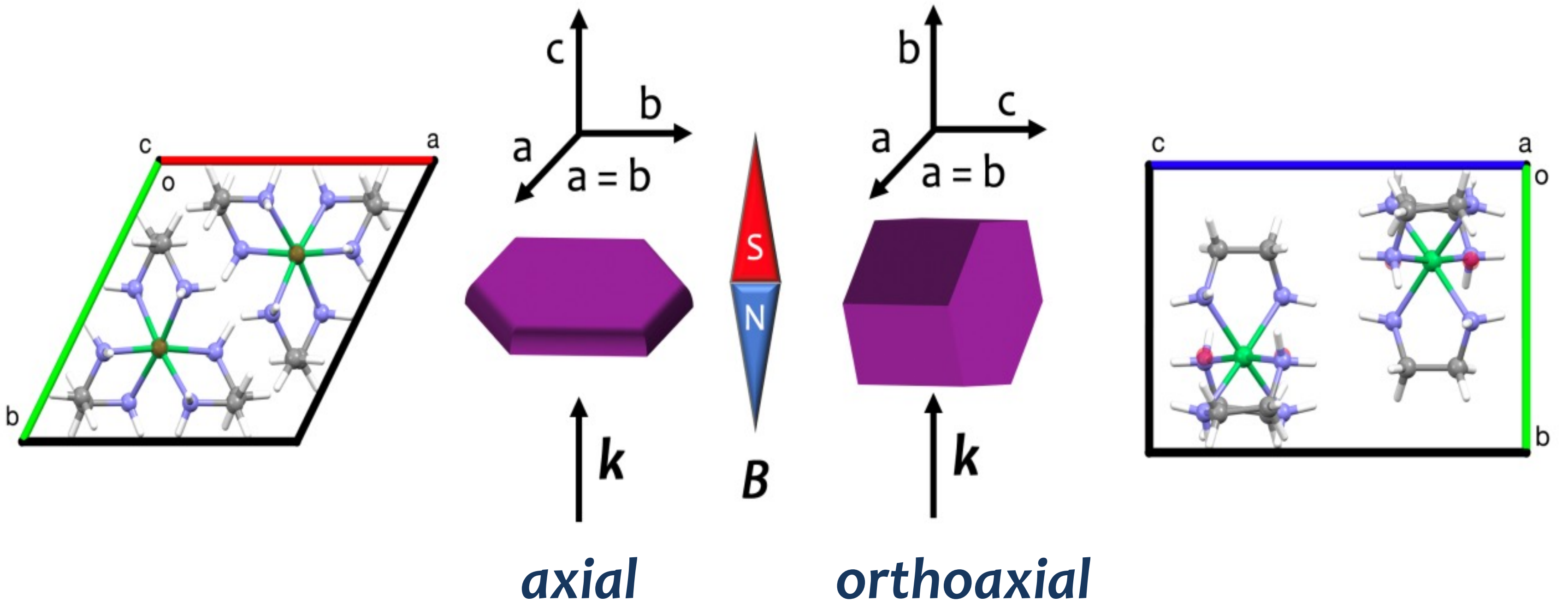


- ✓ Linear variation of ΔA_{MChD} with ***B*** *(low fields)*
- ✓ Linear variation of ΔA_{MChD} with *1/T (Curie Law)*

M. Atzori *et al. Sci. Adv.* **2021,** 7, eabg2859

3. MChD in Enantiopure Magnetic Complexes

MChD measurements as a function of the crystal orientation



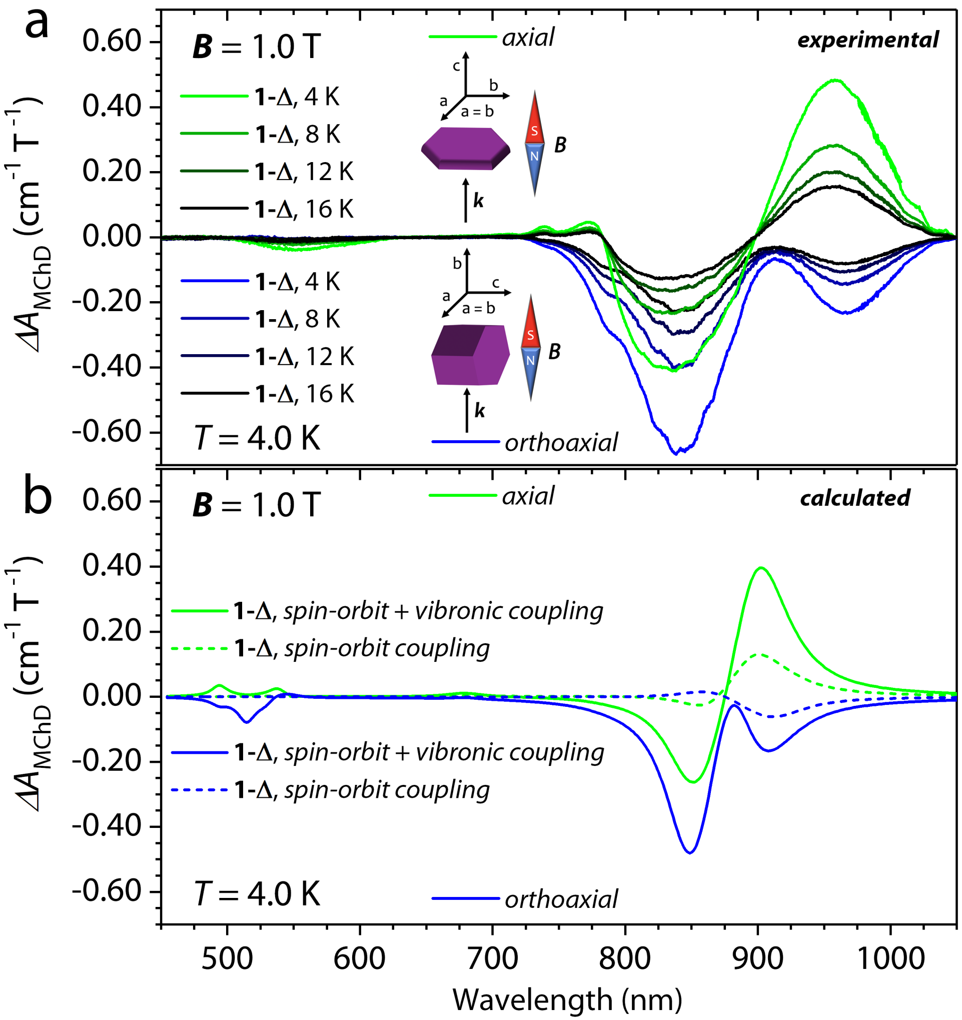
M. Atzori *et al. Sci. Adv.* **2021,** 7, eabg2859

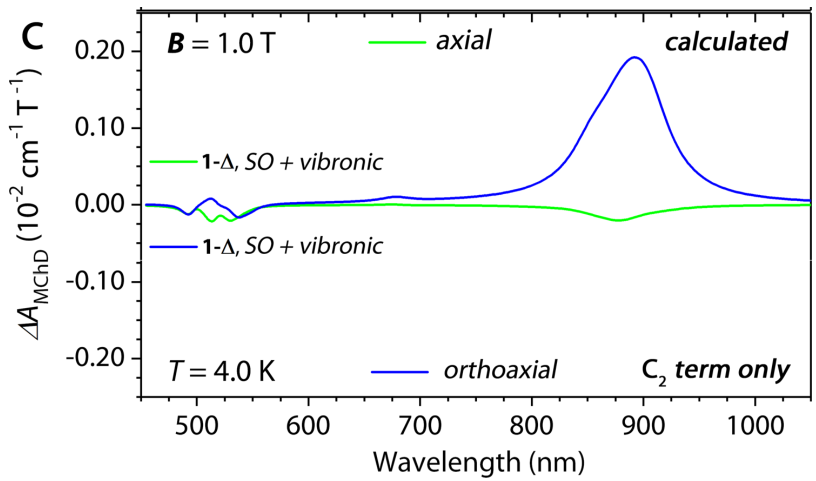
3. MChD in Enantiopure Magnetic Complexes

Experimental and Calculated MChD spectra

Collaboration with

Prof. J. Autschbach
U.S.A.





Electric dipole-magnetic dipole

$$C_1 = \frac{1}{d}\sum_{\alpha,\beta,\gamma} \epsilon_{\alpha,\beta,\gamma} \sum_n m^{\alpha}_{n,n} \mathrm{Re}\left[\mu^{\beta}_{n,j} m^{\gamma}_{j,n}\right]$$

$$C_2 = \frac{\omega}{15d}\sum_{\alpha,\beta}\sum_n m^{\alpha}_{n,n} \mathrm{Im}\left[3\mu^{\beta}_{n,j}\Theta^{\beta,\alpha}_{j,n} - \mu^{\alpha}_{n,j}\Theta^{\beta,\beta}_{j,n}\right]$$

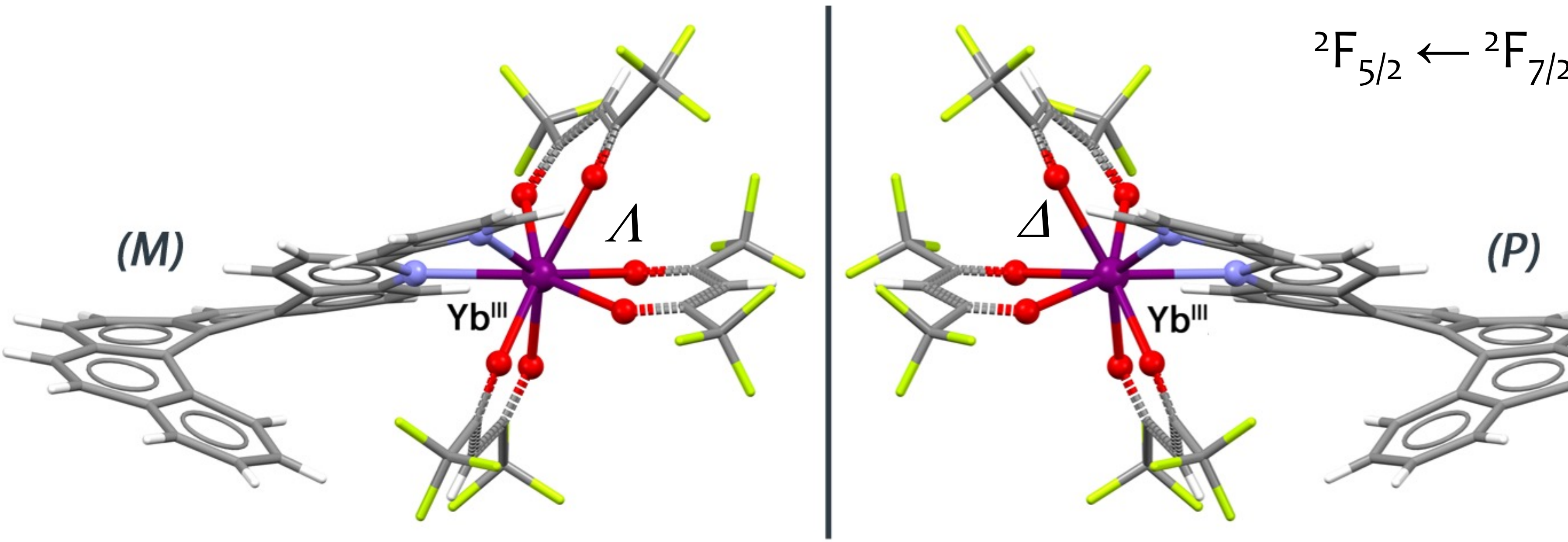
Electric dipole-electric quadrupole

M. Atzori *et al. Sci. Adv.* **2021**, 7, eabg2859

Based on MChD Theory
Barron and Vbranchich, **1984**

4. MChD in Chiral Ytterbium Complexes

Motivation: Correlate MChD to the character of electronic transitions



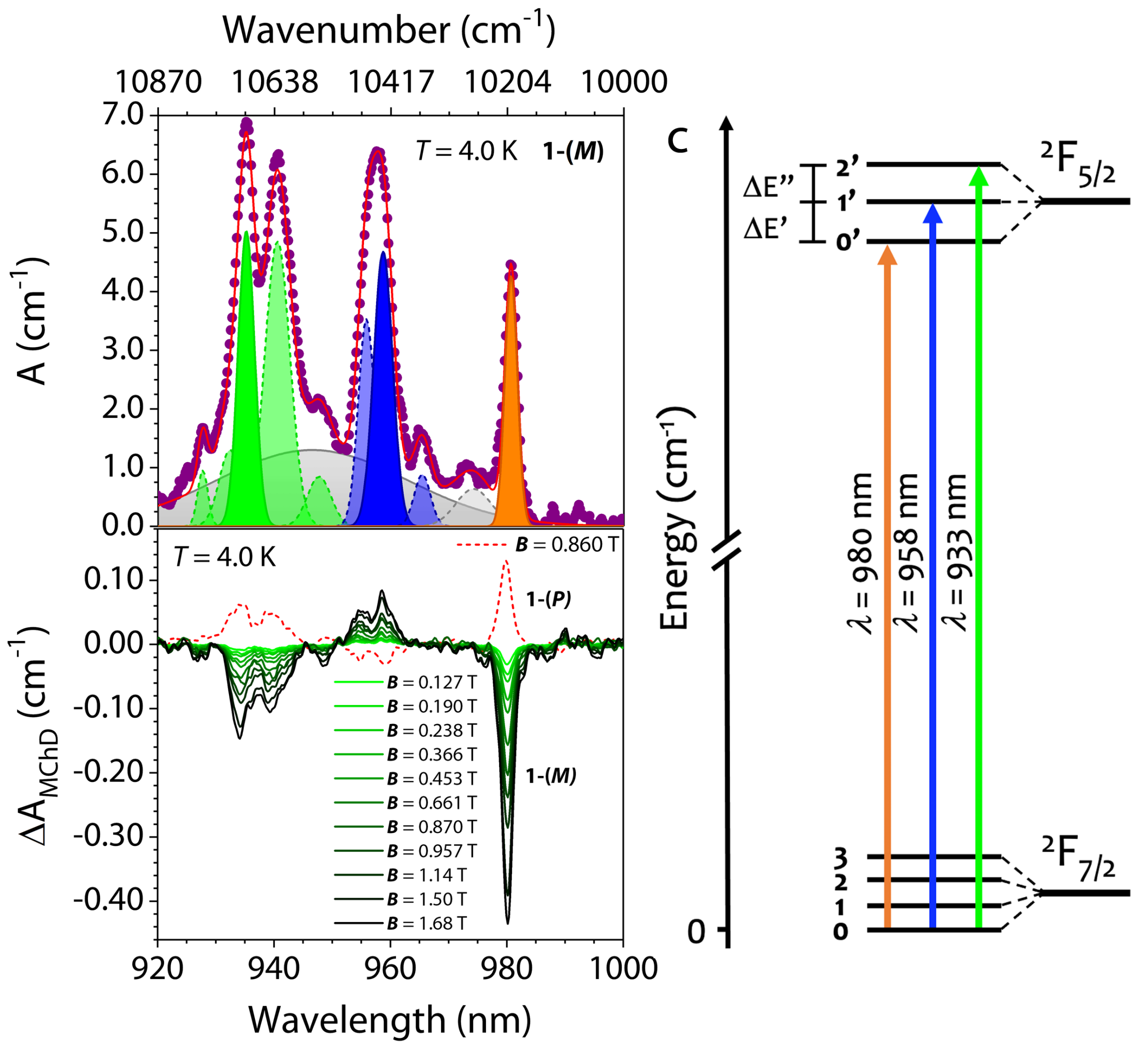
[[**Yb^{III}**((*X*)-**L**)(*hfac*)$_3$] (*X* = *P*, *M*)

J. Am. Chem. Soc. **2021**, *143*, 2671–2675

With: F. Pointillart, J. Crassous, B. Le Guennic (Univ. Rennes)

4. MChD in Chiral Ytterbium Complexes

First Observation of MChD through Light Absorption in Lanthanides

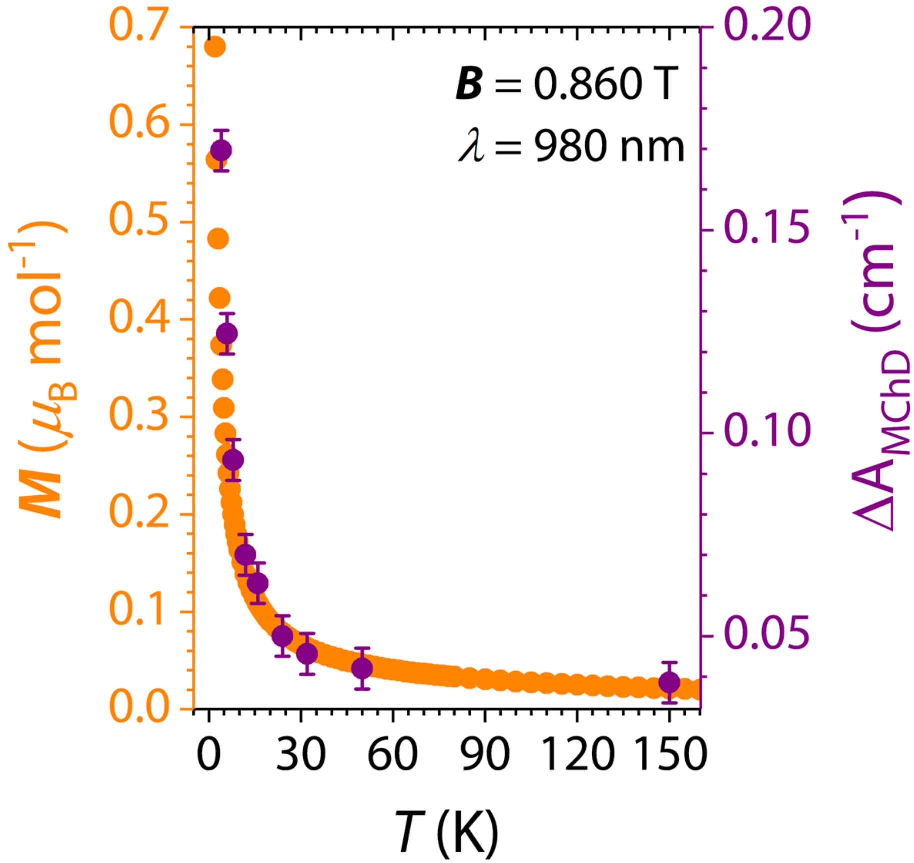


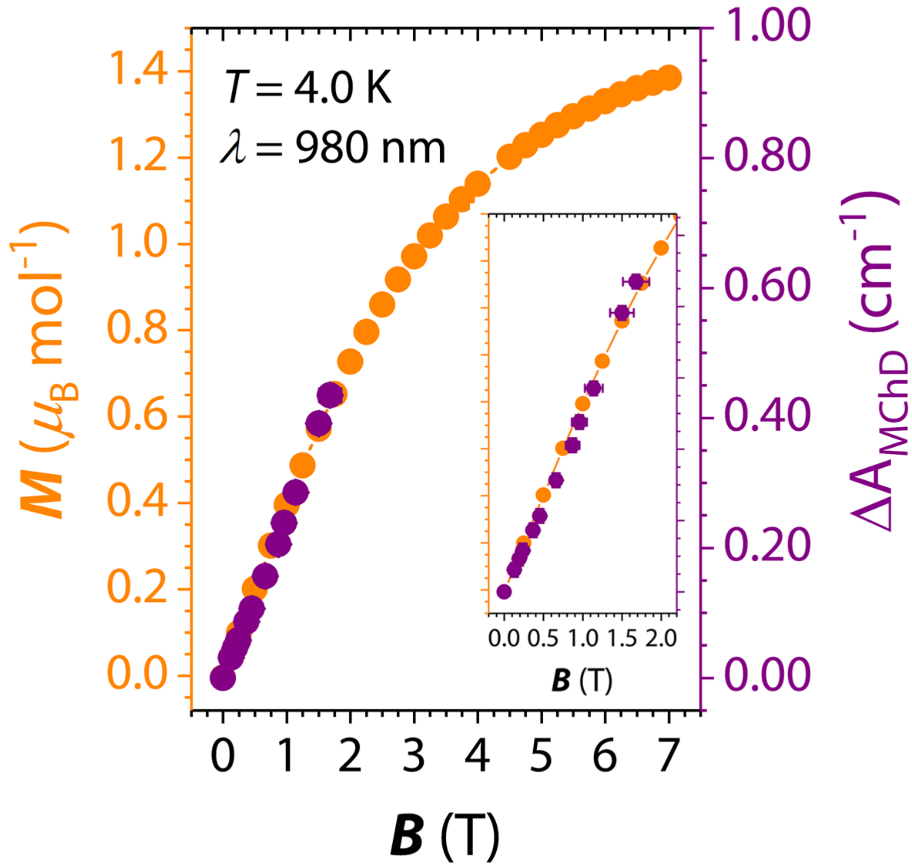
- ✓ One well-defined *f-f* electronic transition with $|\Delta J| = 1$
- ✓ Absorption spectrum split by Crystal Field and Vibronic Coupling
- ✓ Strong signal associated to to the high SOC, local chirality and MD character of the electronic transition

J. Am. Chem. Soc. **2021**, *143*, 2671–2675

4. MChD in Chiral Ytterbium Complexes

Temperature and Field dependence of MChD



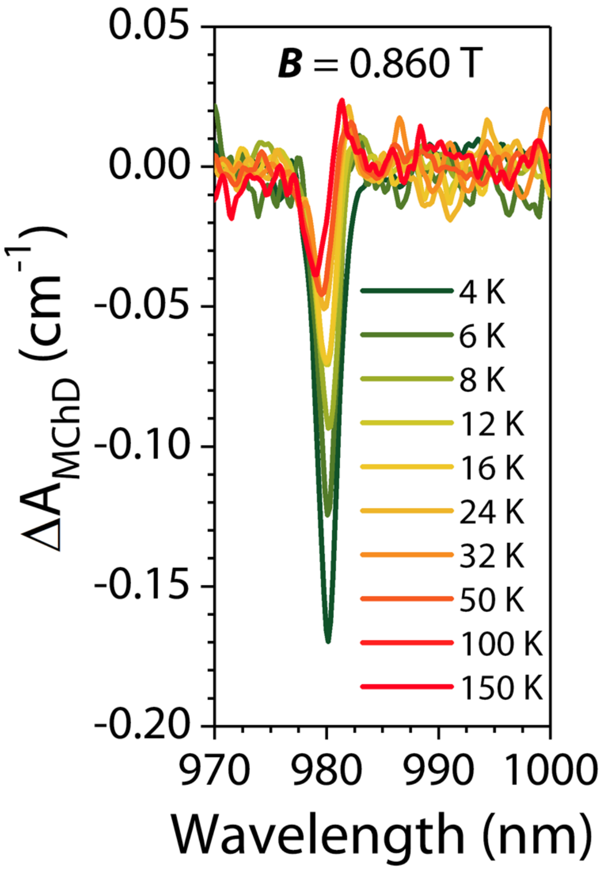


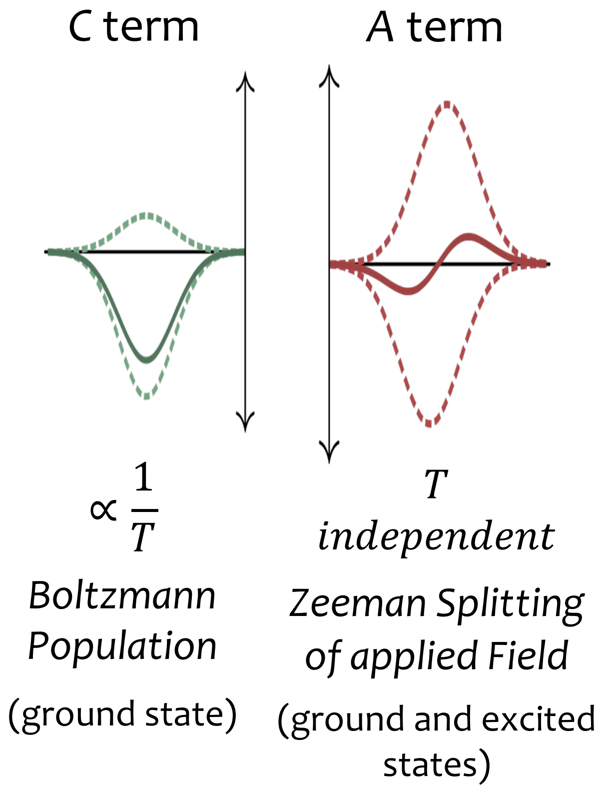
$$\Delta A^{\Delta/\Lambda} \propto \boldsymbol{M}(T, \boldsymbol{B})$$

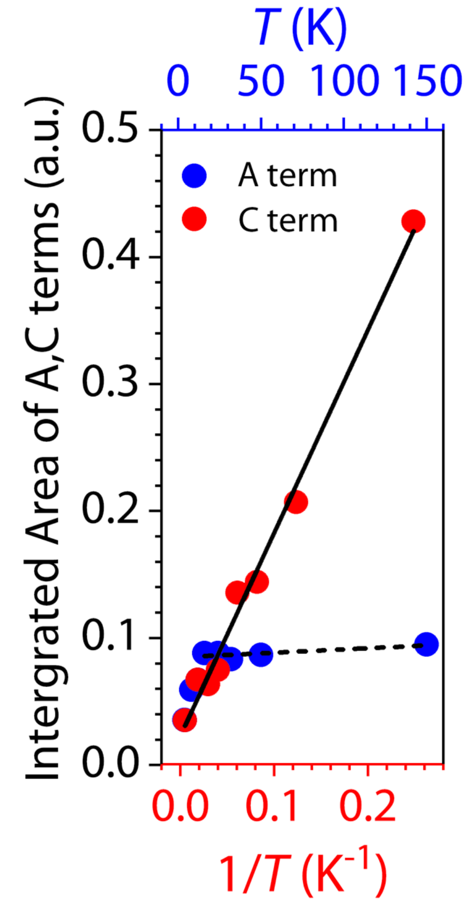
J. Am. Chem. Soc. **2021,** *143,* 2671–2675

4. MChD in Chiral Ytterbium Complexes

Temperature dependence of MChD signals







A and C MChD terms and *T* dependence as predicted by MChD theory

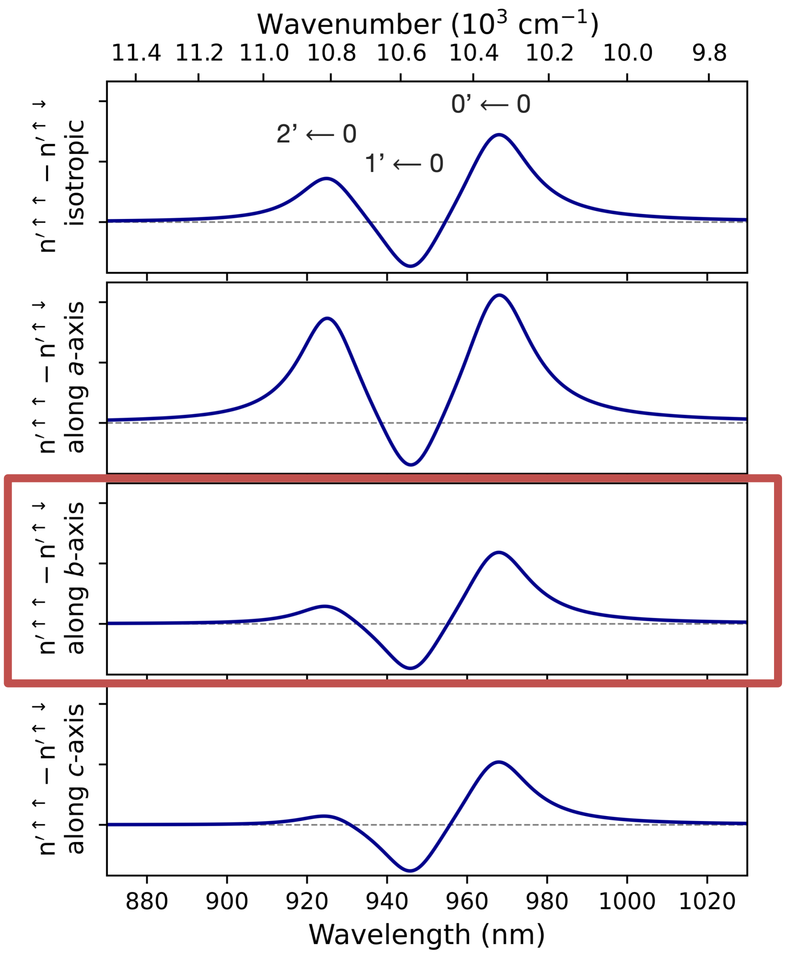
J. Am. Chem. Soc. **2021,** *143,* 2671–2675

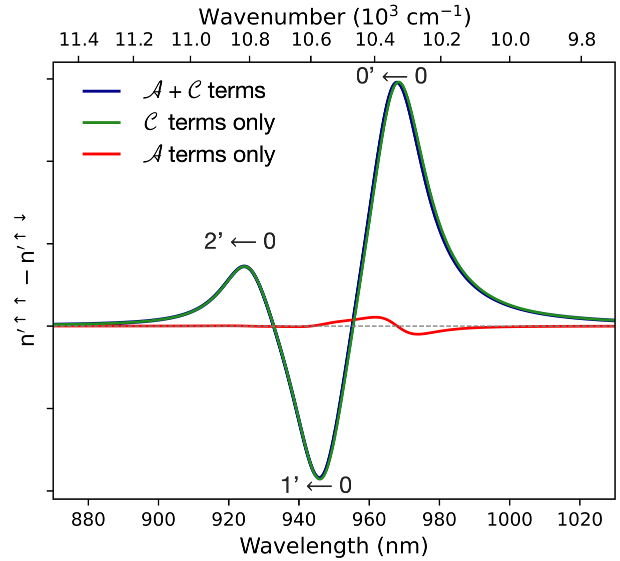
4. MChD in Chiral Ytterbium Complexes

Theoretical calculations

With : B. Le Guennic & M. Gresser
(Rennes – France)

Very good agreement with the experiments





SA-CAS(13,7)PT2/RASSI-SO

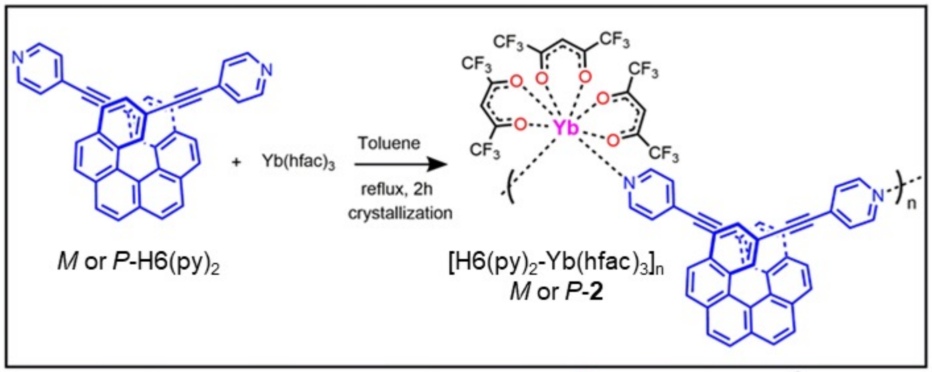
Based on MChD Theory
Barron and Vbranchich, **1984**

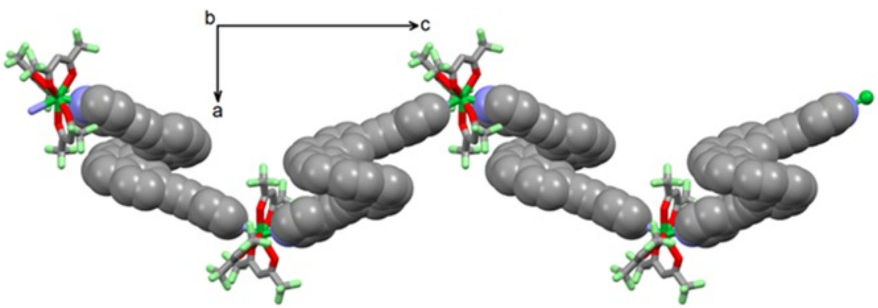
$$n'^{\uparrow\uparrow} - n'^{\uparrow\downarrow} \approx \frac{2\,\mu_0\,c\,N B_z}{3}\left(2(\omega_{jn}^2 + \omega^2) f g \mathcal{A}(G) - 4\,\omega_{jn}\,\omega f g \mathcal{A}(A') + \omega_{jn}\,g\frac{\mathcal{C}(G)}{k_B T} - \omega g \frac{\mathcal{C}(A')}{k_B T}\right)$$

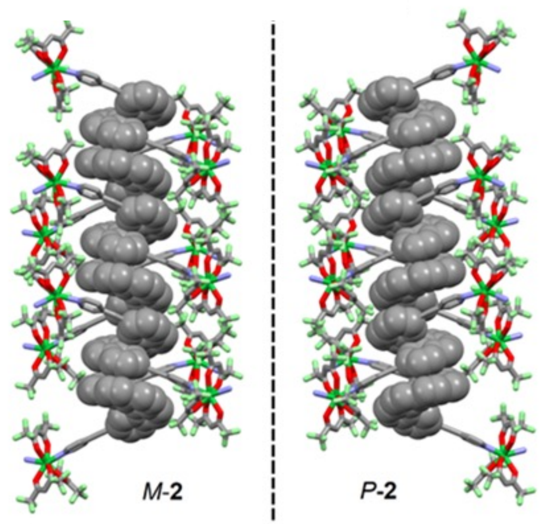
Unpublished Results

4. MChD in Chiral Ytterbium Complexes

MChD in chiral coordination polymers







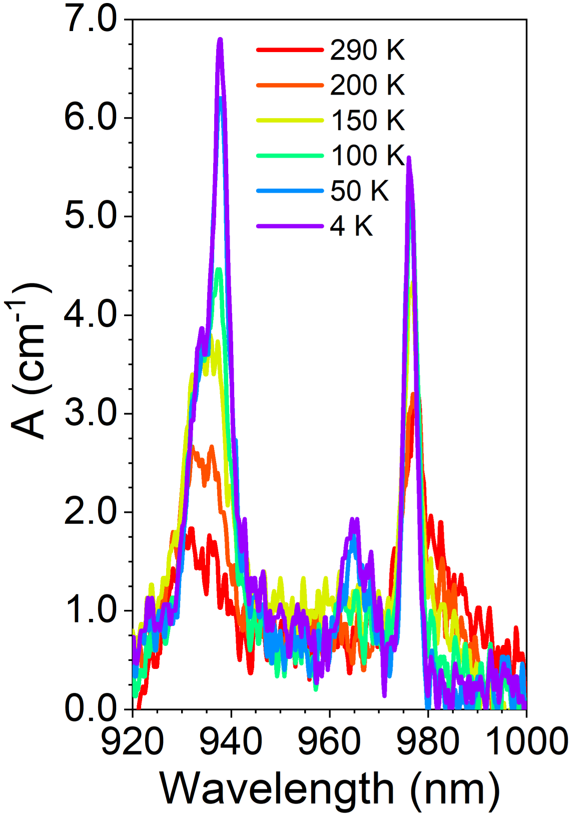
Slow magnetic relaxation and CPL at room temperature

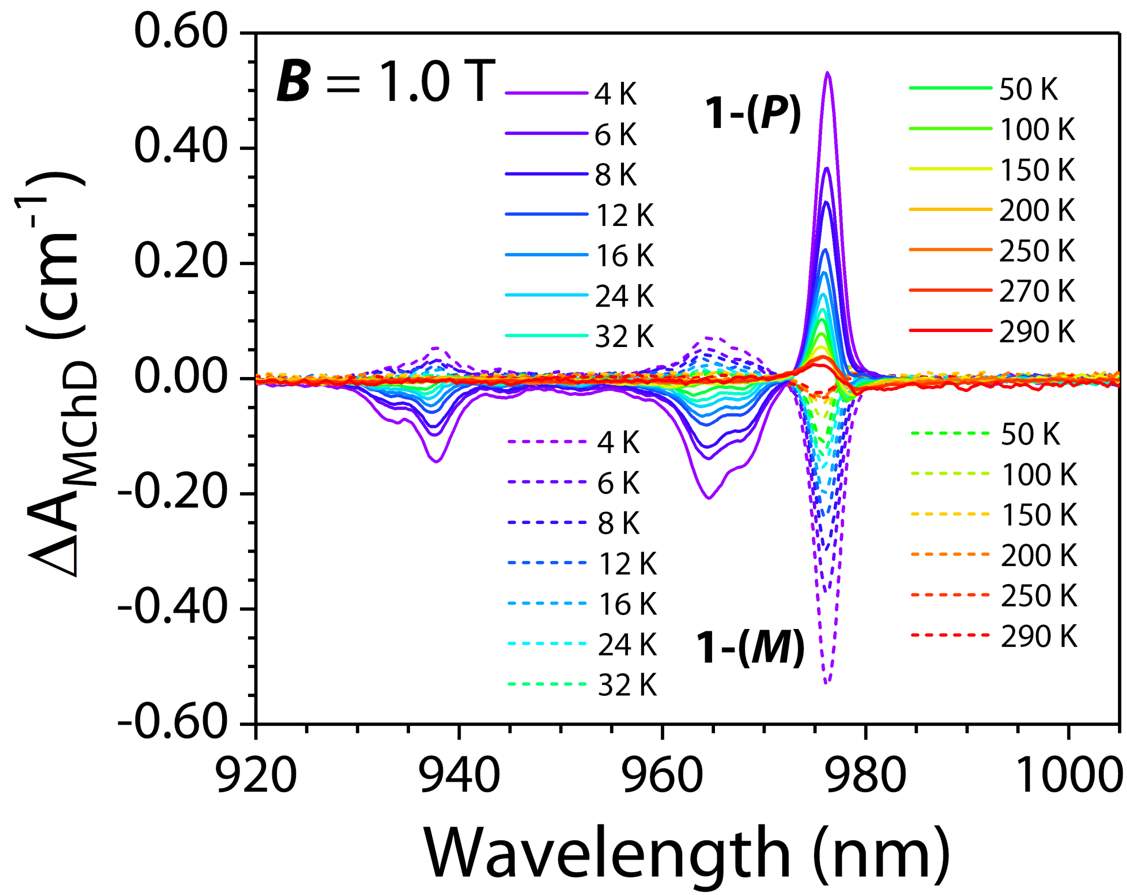
With: F. Pointillart, J. Crassous, B. Le Guennic (Univ. Rennes)

Angew. Chem. Int. Ed. **2022**, e202215558K

4. MChD in Chiral Ytterbium Complexes

Strong MChD, detectable up to room temperature





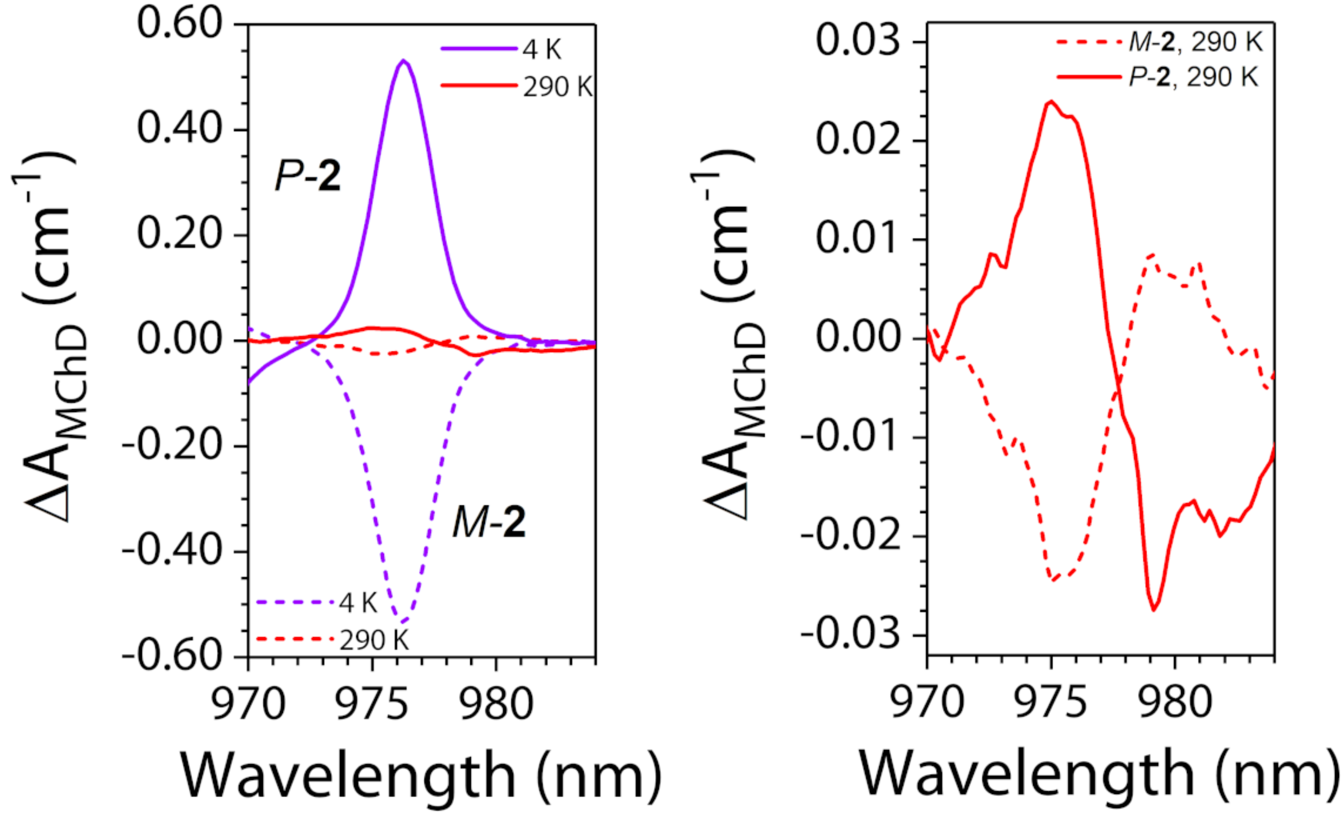
g_{MChD} of 0.20 T^{-1} at T = 4.0 K

$$g_{MChD} = \frac{\left(A(\boldsymbol{B}\uparrow\uparrow\boldsymbol{k}) - A(\boldsymbol{B}\downarrow\uparrow\boldsymbol{k})\right)}{½\left(A(\boldsymbol{B}\uparrow\uparrow\boldsymbol{k}) + A(\boldsymbol{B}\downarrow\uparrow\boldsymbol{k})\right)\boldsymbol{B}}$$

Angew. Chem. Int. Ed. **2022**, e202215558K

4. MChD in Chiral Ytterbium Complexes

Room temperature MChD

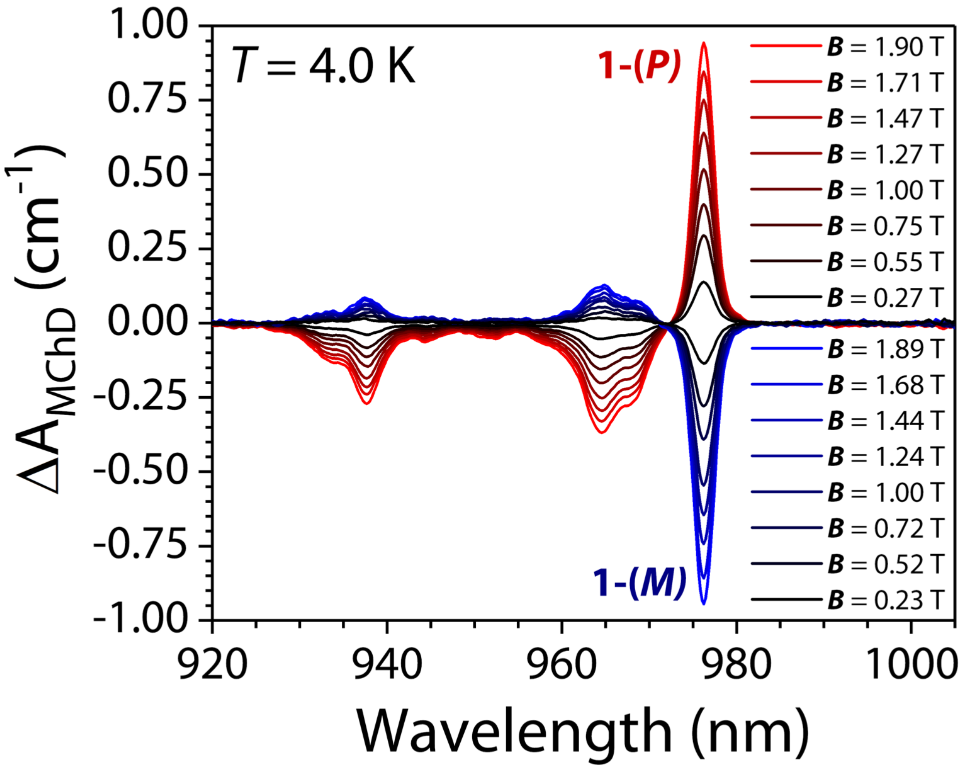


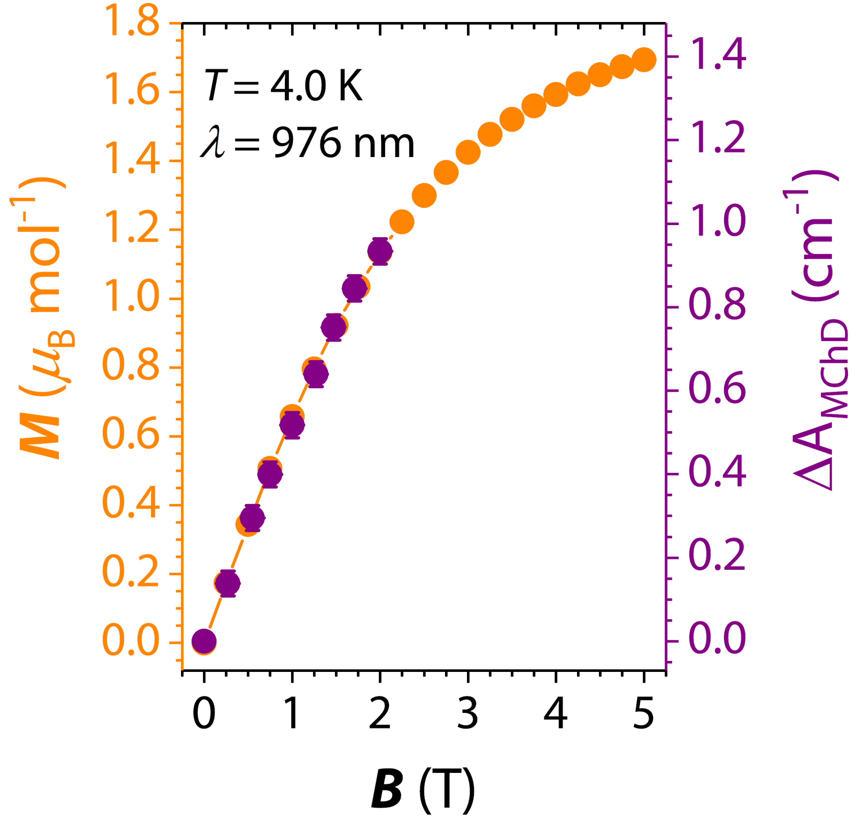
Low temperature MChD C term and room temperature MChD *A* term

Angew. Chem. Int. Ed. **2022,** e202215558K

4. MChD in Chiral Ytterbium Complexes

Magnetic Field dependence of MChD





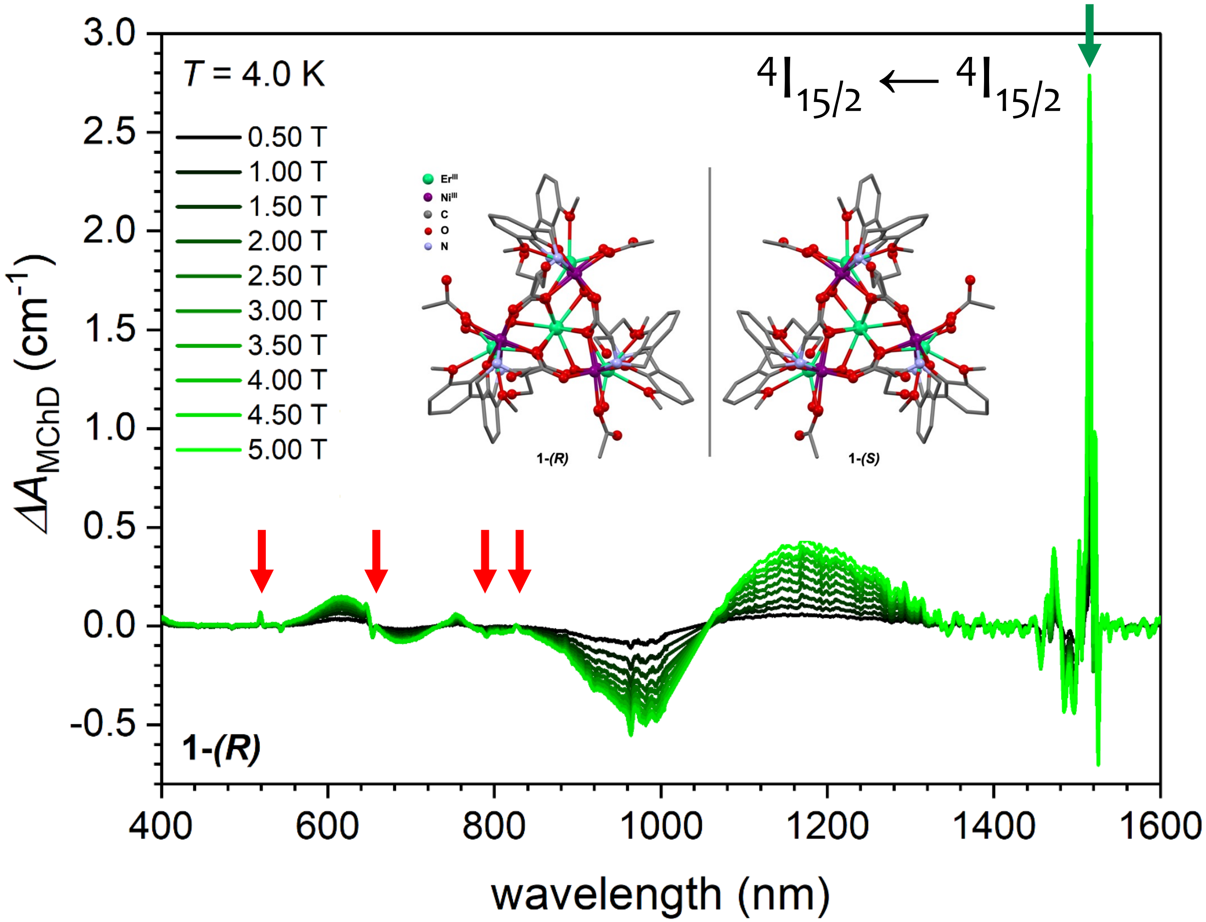
Magneto-chiral optical data perfectly follow the magnetization

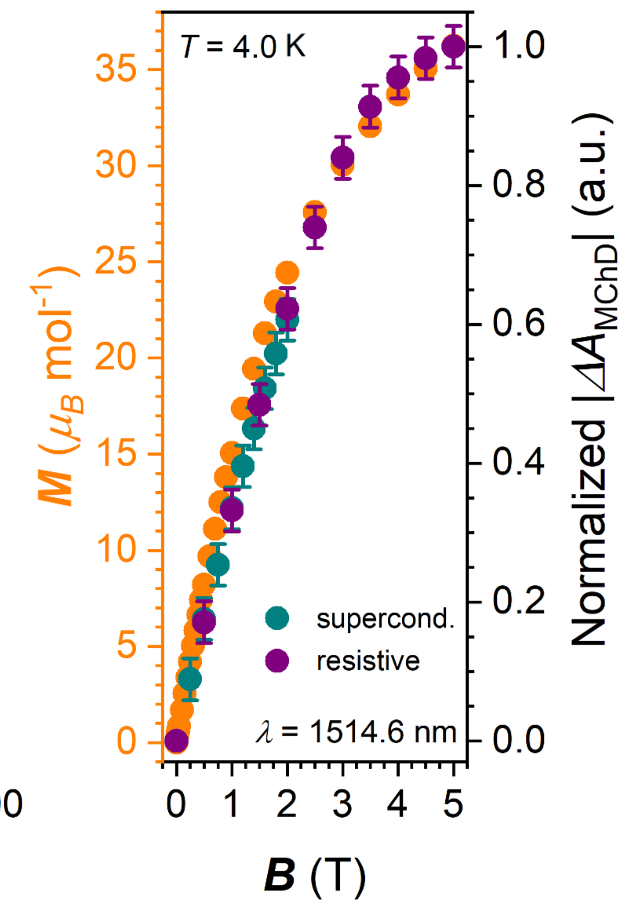
Angew. Chem. Int. Ed. **2022**, e202215558K

5. MChD in Chiral Erbium Complexes

Key-role of <u>magnetic-dipole allowed transitions</u> unambiguously determined

With: X.-J. Kong (Xiamen – China)





J. Am. Chem. Soc. **2024**, *146*, 16389–16393

5. MChD in Chiral Erbium Complexes

Selection rules for strong MChD-active electronic transitions in lanthanides complexes

With: F. Zinna, F. Pineider, L. Di Bari (University of Pisa)

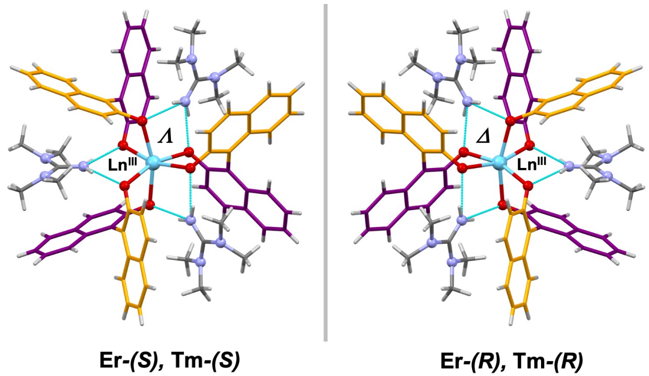


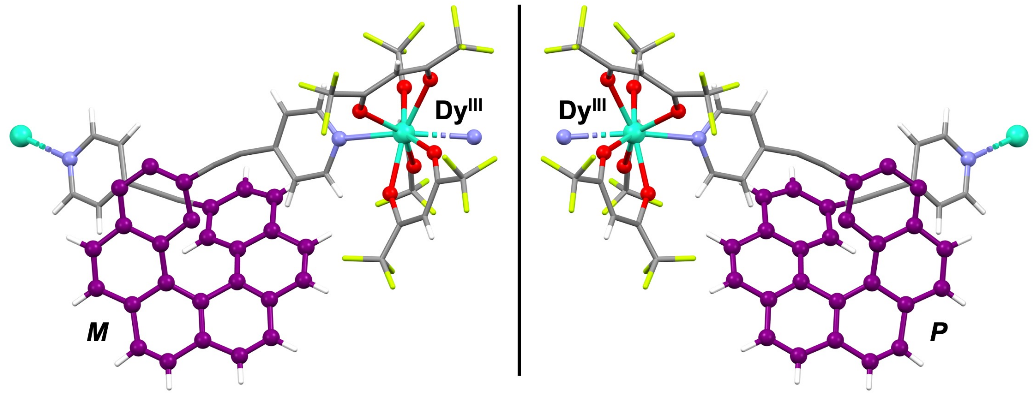
Table 1: Assignment of the Er^{III} and Tm^{III} absorption peaks, transition properties, Richardson's classification[38] and g_{MChD} values (T=4.0 K and $\boldsymbol{B}$=1.0 T).

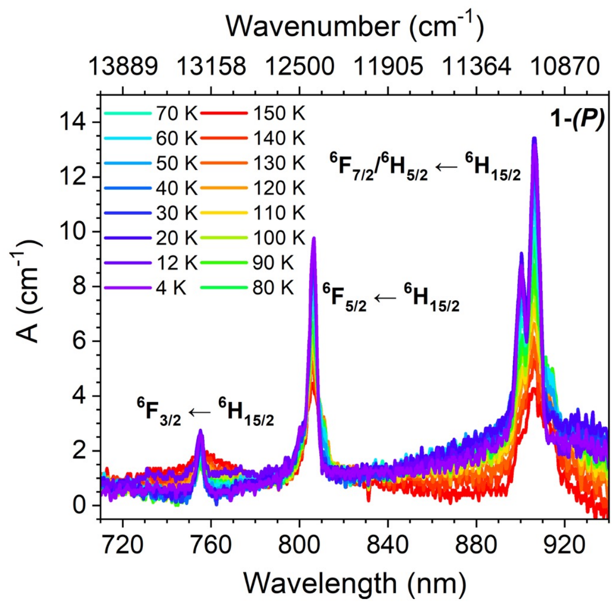
Compound	λ (nm)	Electronic transition	Transition properties	Richardson classification	g_{MChD} (T^{-1}), λ (nm)
Er	475–495	$^4F_{7/2}\leftarrow{}^4I_{15/2}$	$\Delta J=4, \Delta L=3, \Delta S=0$	E-I, R-II, D-III	0.001(1), 450.2
Er	505–530	$^2H_{11/2}\leftarrow{}^4I_{15/2}$	$\Delta J=2, \Delta L=1, \Delta S=1$	E-III, R-III, D-II	0.001(1), 522.6
Er	540–560	$^4S_{3/2}\leftarrow{}^4I_{15/2}$	$\Delta J=6, \Delta L=6, \Delta S=0$	E-I, R-II, D-III	0.004(1), 546.3
Er	640–670	$^4F_{9/2}\leftarrow{}^4I_{15/2}$	$\Delta J=3, \Delta L=3, \Delta S=0$	E-III, R-III, D-II	0.03(1), 658.0
Er	780–820	$^4I_{9/2}\leftarrow{}^4I_{15/2}$	$\Delta J=3, \Delta L=0, \Delta S=0$	E-III, R-III, D-II	0.03(1), 800.1
Er	960–1000	$^4I_{11/2}\leftarrow{}^4I_{15/2}$	$\Delta J=2, \Delta L=0, \Delta S=0$	E-I, R-II, D-III	0.03(1), 967.2
Er	**1450–1550**	$\boldsymbol{^4I_{13/2}\leftarrow{}^4I_{15/2}}$	$\boldsymbol{\Delta J=1, \Delta L=0, \Delta S=0}$	**E-I, R-I, D-II**	**0.12(1), 1514.6**
Tm	650–700	$^3F_3\leftarrow{}^3H_6$	$\Delta J=3, \Delta L=2, \Delta S=0$	E-III, R-III, D-II	0.005(1), 685.3
Tm	760–805	$^3H_4\leftarrow{}^3H_6$	$\Delta J=2, \Delta L=0, \Delta S=0$	E-I, R-II, D-III	0.002(1), 794.7
Tm	**1130–1230**	$\boldsymbol{^3H_5\leftarrow{}^3H_6}$	$\boldsymbol{\Delta J=1, \Delta L=0, \Delta S=0}$	**E-I, R-I, D-II**	**0.047(1), 1213.5**

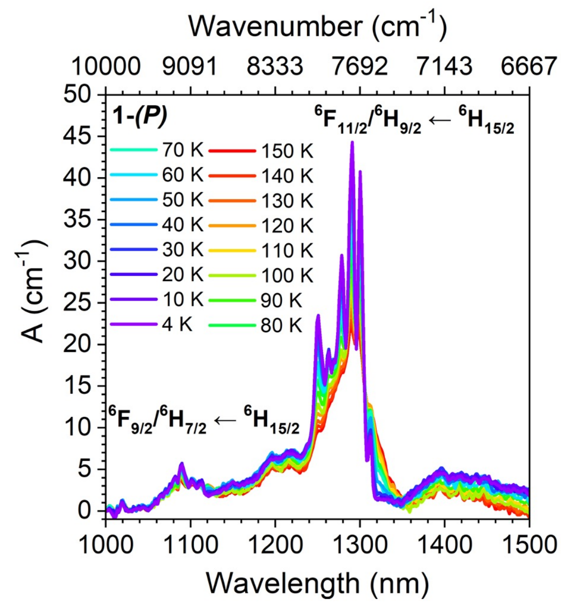
Angew. Chem. Int. Ed. **2024**, 63, e202412521

6. MChD in Chiral Dysprosium Complexes

With: F. Pointillart, J. Crassous,
B. Le Guennic (Rennes – France)



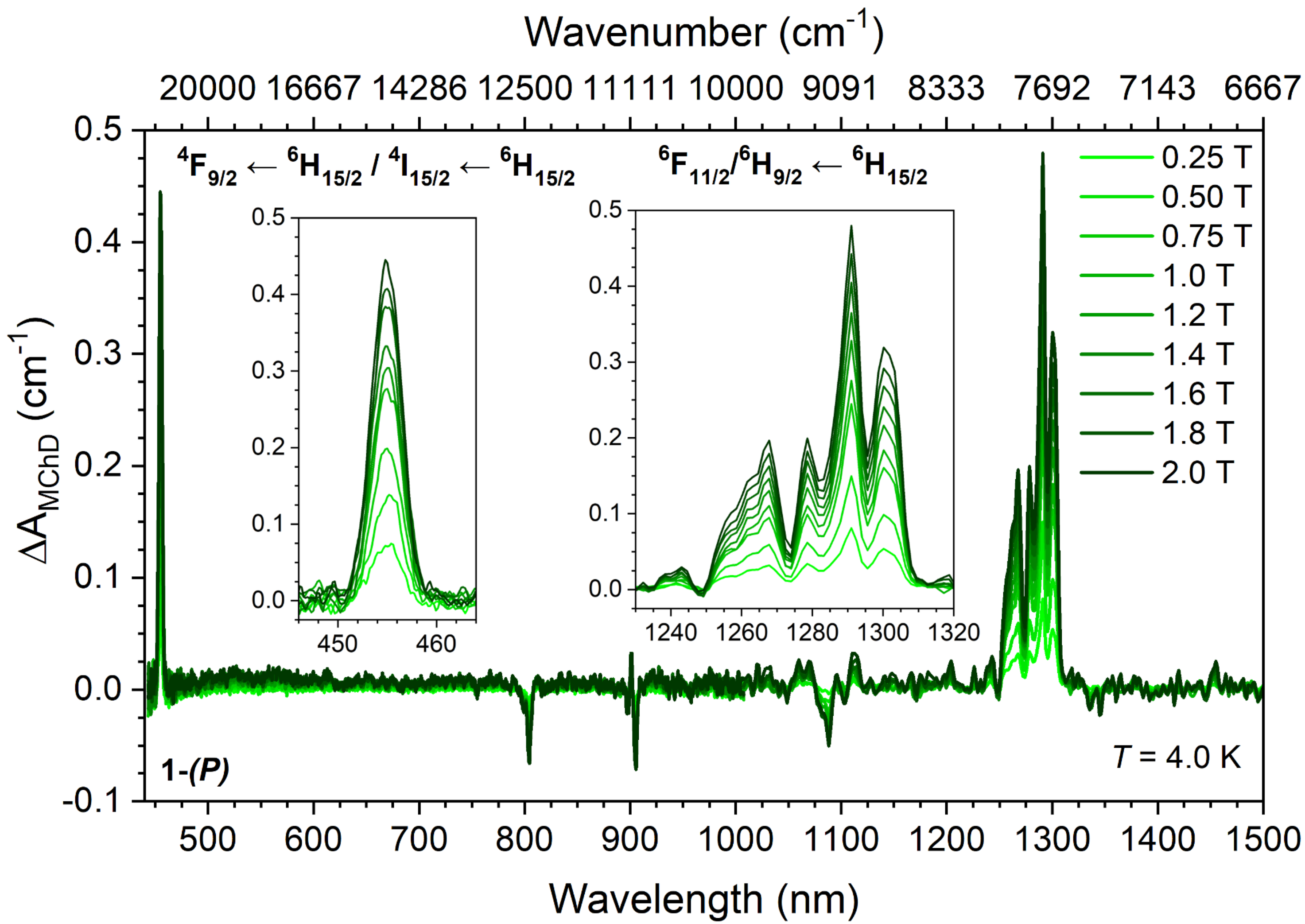




Inorg. Chem. **2023**, *62*, *17583*

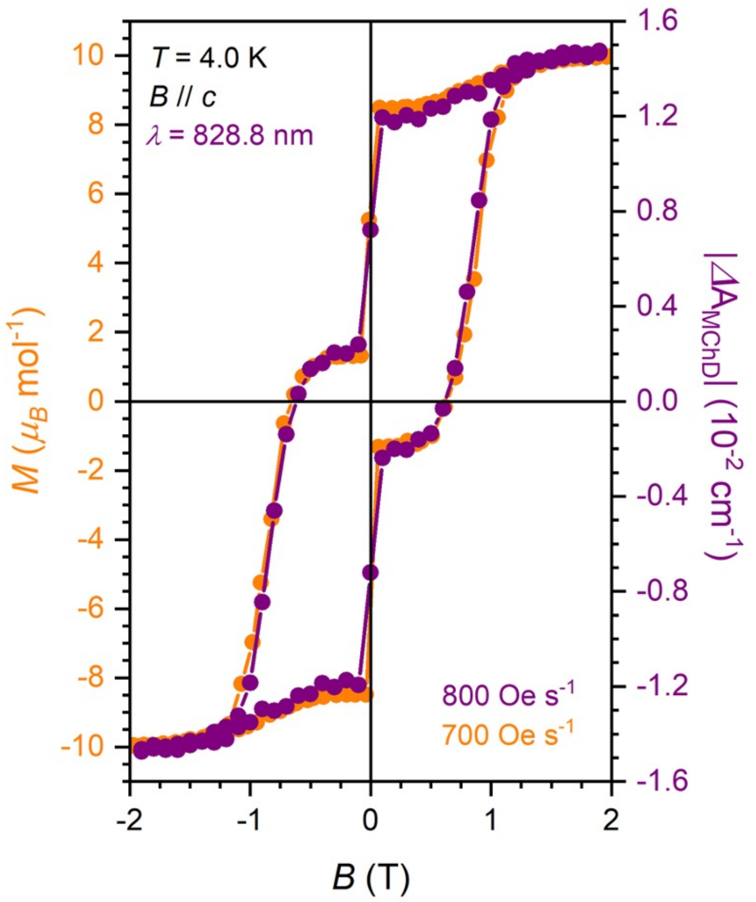
6. MChD in Chiral Dysprosium Complexes

Magnetic Field dependence of MChD



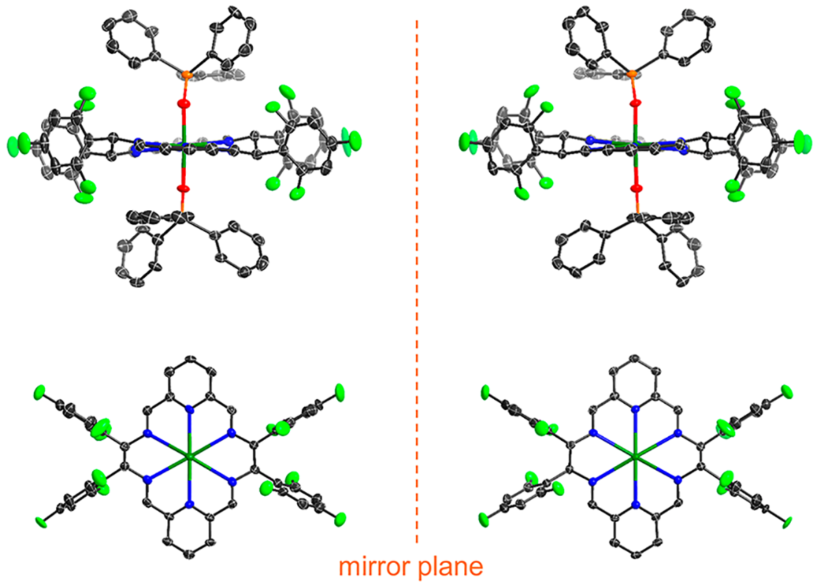
Inorg. Chem. **2023**, *62*, *17583*

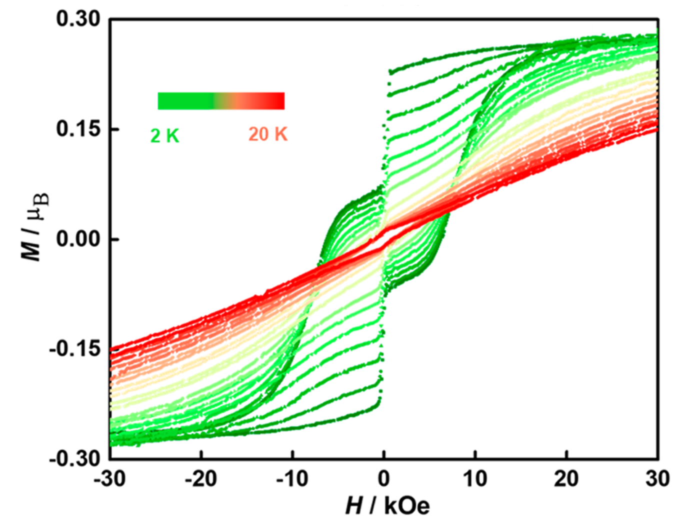
Optical Readout of Single-Molecule Magnetic Memories using Unpolarized Light



Requirements and analysis of the literature

Chiral Dy^{III} SMM with open hysteresis at T = 4.0 K





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Communication

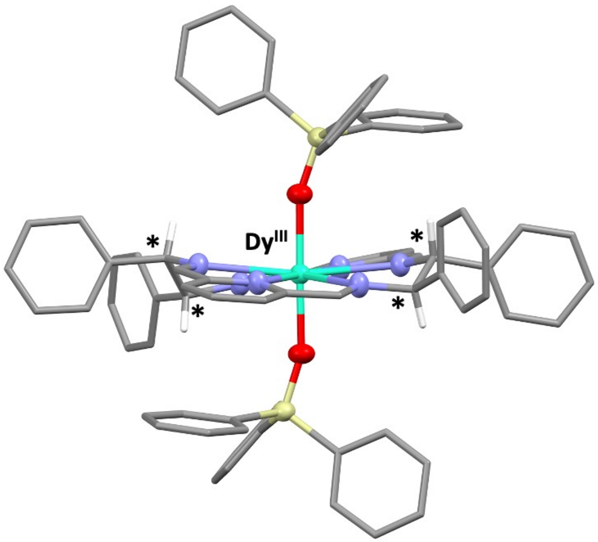
Air-Stable Chiral Single-Molecule Magnets with Record Anisotropy Barrier Exceeding 1800 K

Zhenhua Zhu,# Chen Zhao,# Tingting Feng, Xiaodong Liu, Xu Ying, Xiao-Lei Li, Yi-Quan Zhang,* and Jinkui Tang*

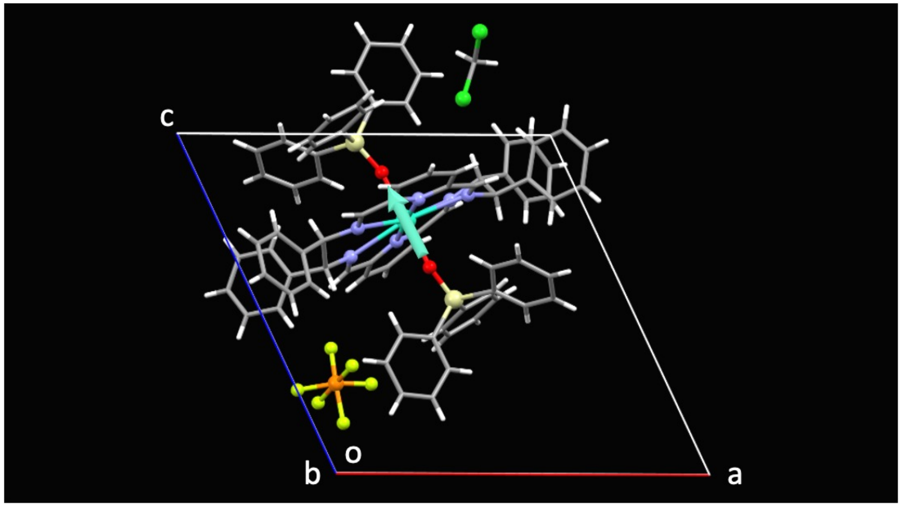
J. Am. Chem. Soc. **2021,** *143,* 10077

Synthesis and Crystallographic Analysis

Hydrogenated analogue of chiral Dy^{III} SMM reported by Tang *et al.*



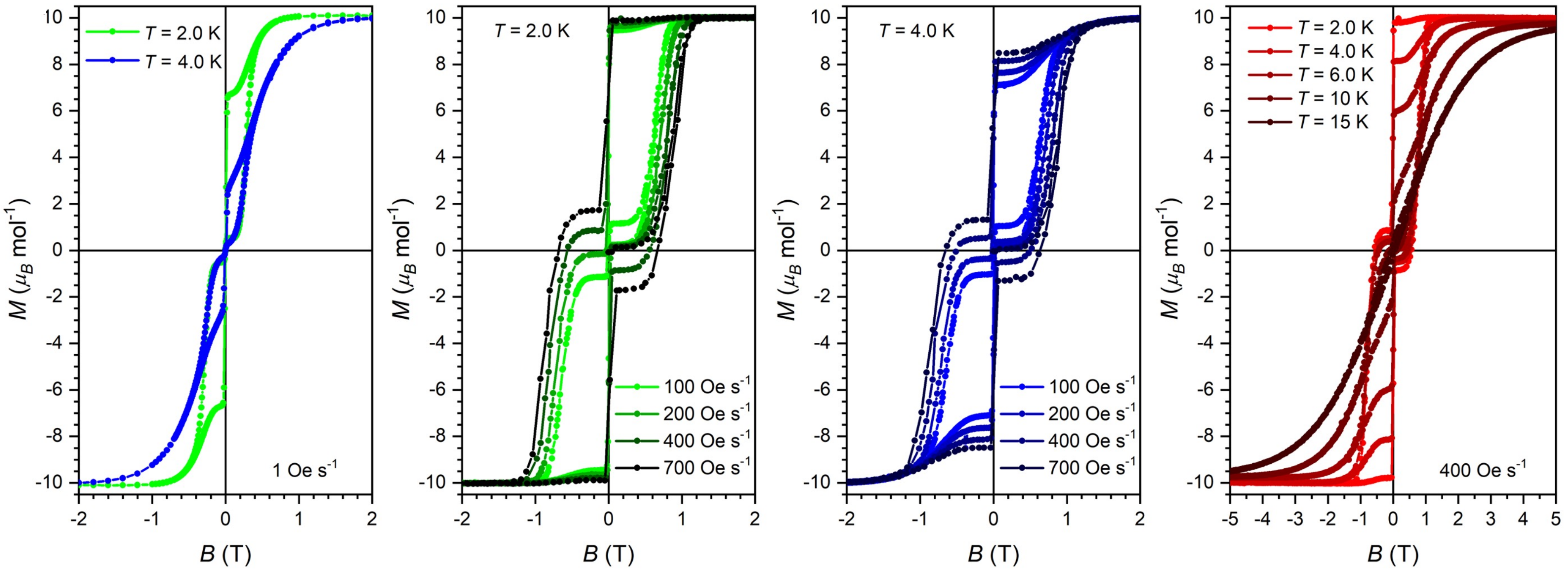
Stable and big single-crystals for orientation-dependent measurements



Easy-axis almost aligned to *c* crystallographic axis

J. Am. Chem. Soc. **2024**, *146*, 23624

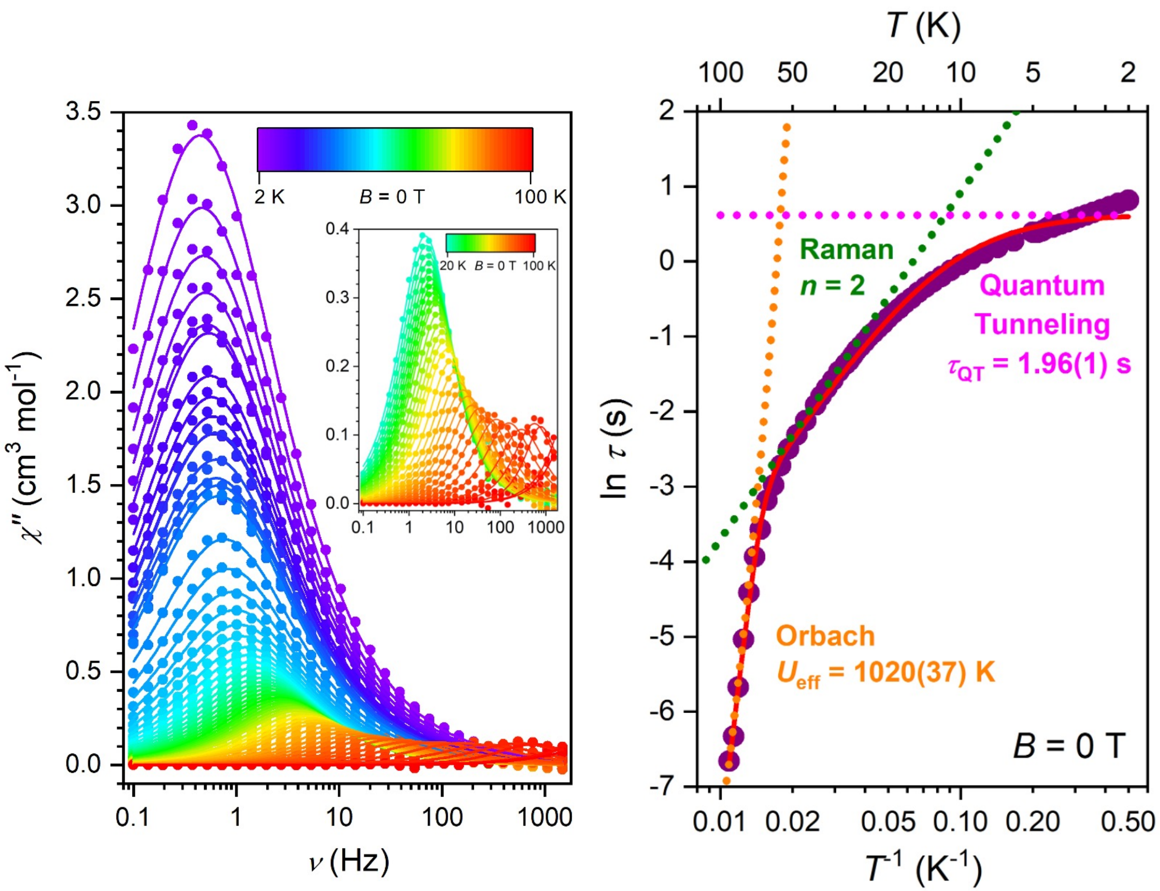
Static Magnetic Properties



Hysteresis cycles as a function of *T* and *B* sweeping rate on oriented single crystals *B*||*c*

J. Am. Chem. Soc. **2024**, *146*, 23624

Dynamic Magnetic Properties



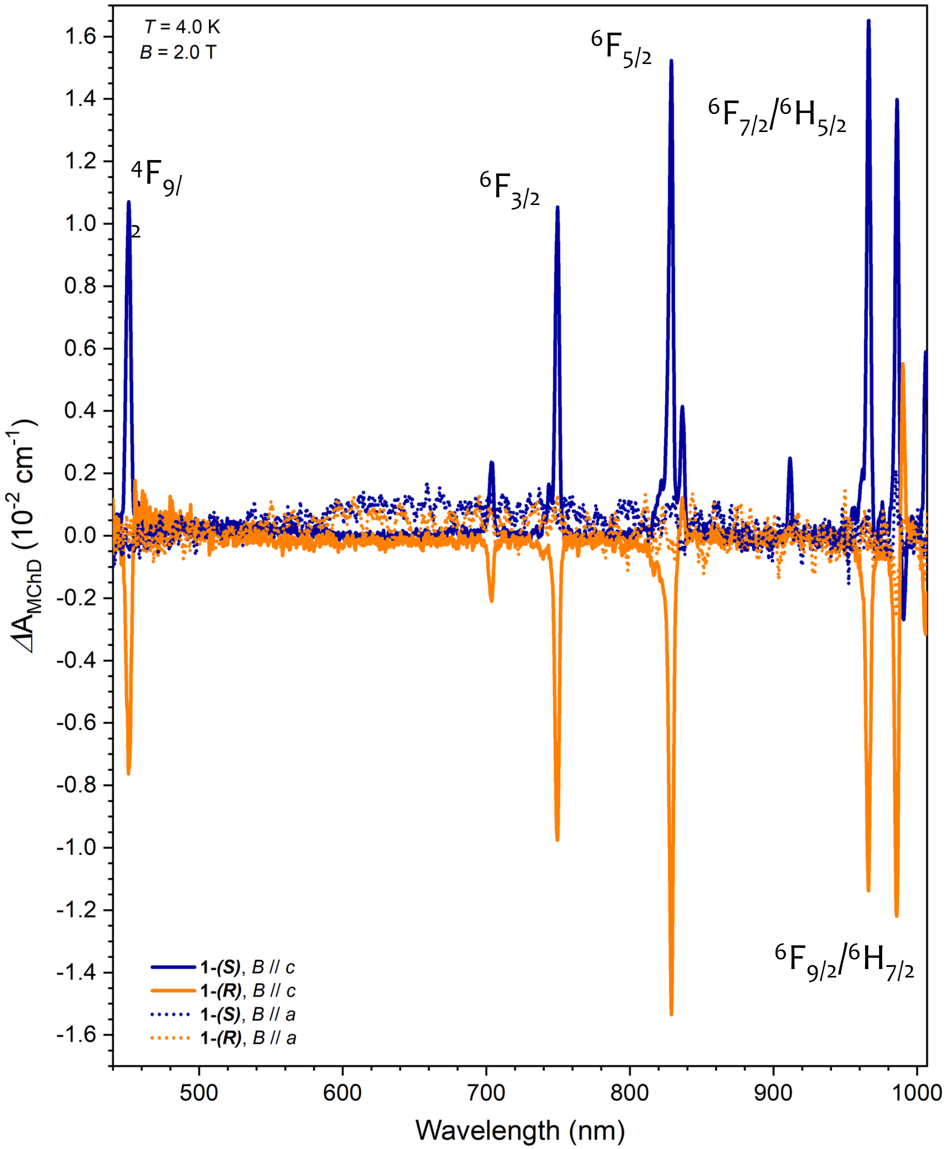
Orbach, Raman and QTM relaxation mechanisms as a function of *T*

U_{eff} ca. 1000 K

$$\tau^{-1} = \tau_{\mathrm{QT}}^{-1} + CT^{n} + \tau_0^{-1}\, exp^{\left(\frac{U_{eff}}{k_B}\right)}$$

J. Am. Chem. Soc. **2024**, 146, 23624

MChD Properties



$$\Delta A(v, T, B) \propto \tanh\left(\frac{g_{||}\, \boldsymbol{B} \cos\theta}{2\, k_B T}\right)$$

$$\boldsymbol{g_{||} = g_z = ca.\, 20}$$

$$g_{\perp} = g_{x,y} = ca.\, 0$$

λ (nm)	*Electronic transition*	g_{MChD} (T^{-1})	
		1-(*R*)	**1-(*S*)**
749.5	$^6F_{3/2} \leftarrow {}^6H_{15/2}$	0.12(1)	0.11(1)
828.8	$^6F_{5/2} \leftarrow {}^6H_{15/2}$	0.08(1)	0.09(1)
966.0	$^6F_{9/2}/^6H_{7/2} \leftarrow {}^6H_{15/2}$	0.06(1)	0.07(1)
985.7	$^6F_{9/2}/^6H_{7/2} \leftarrow {}^6H_{15/2}$	0.05(1)	0.04(1)

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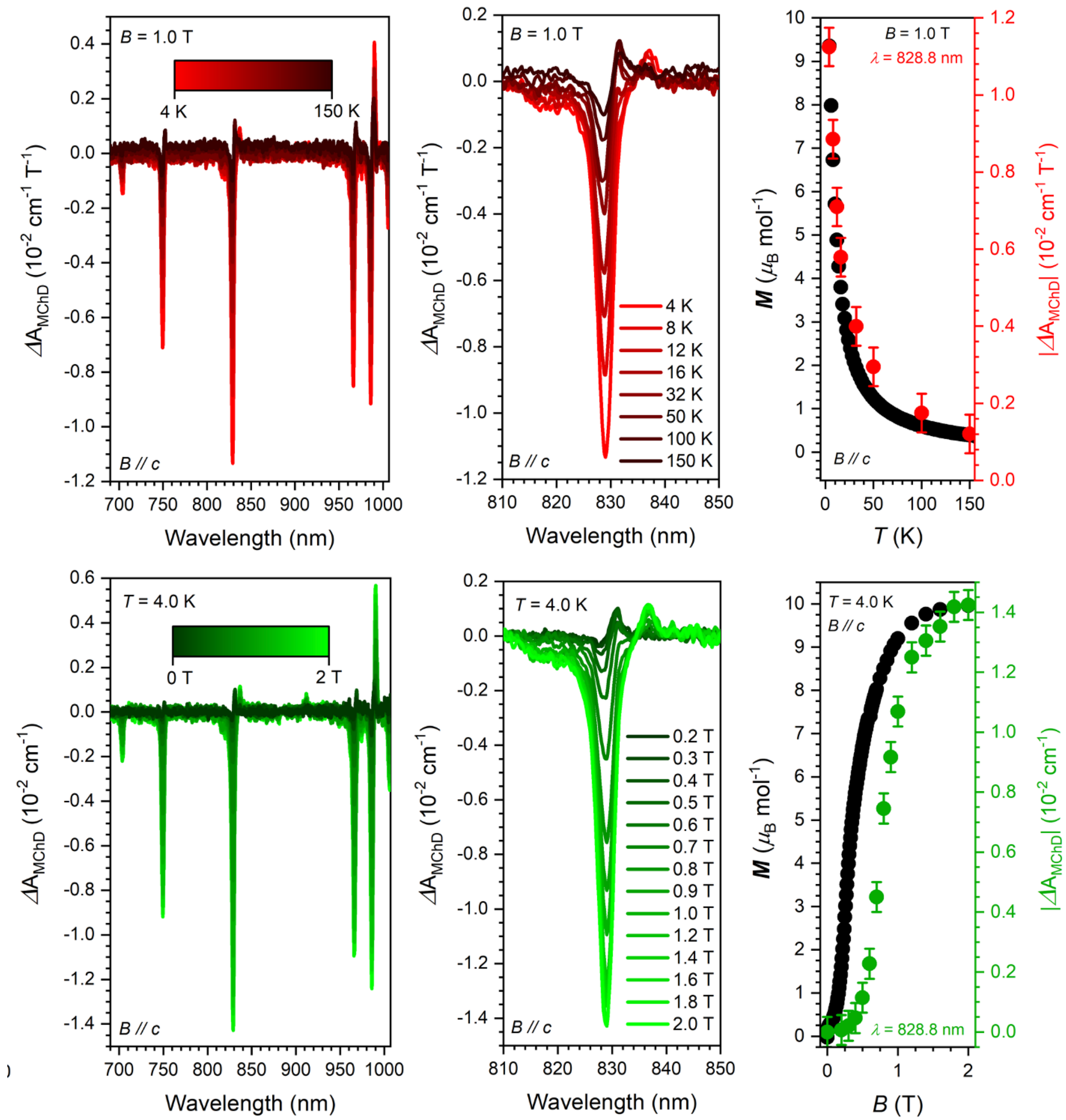
MChD Properties

T dependence

B dependence



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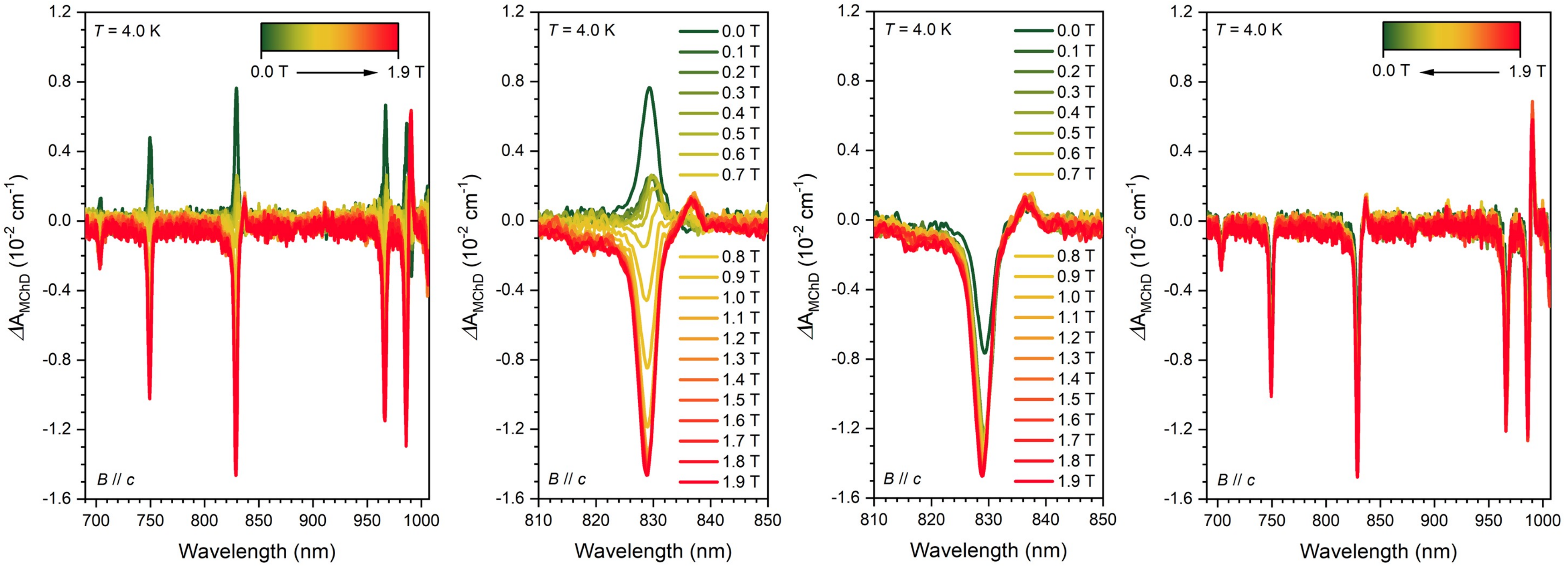
MChD Properties



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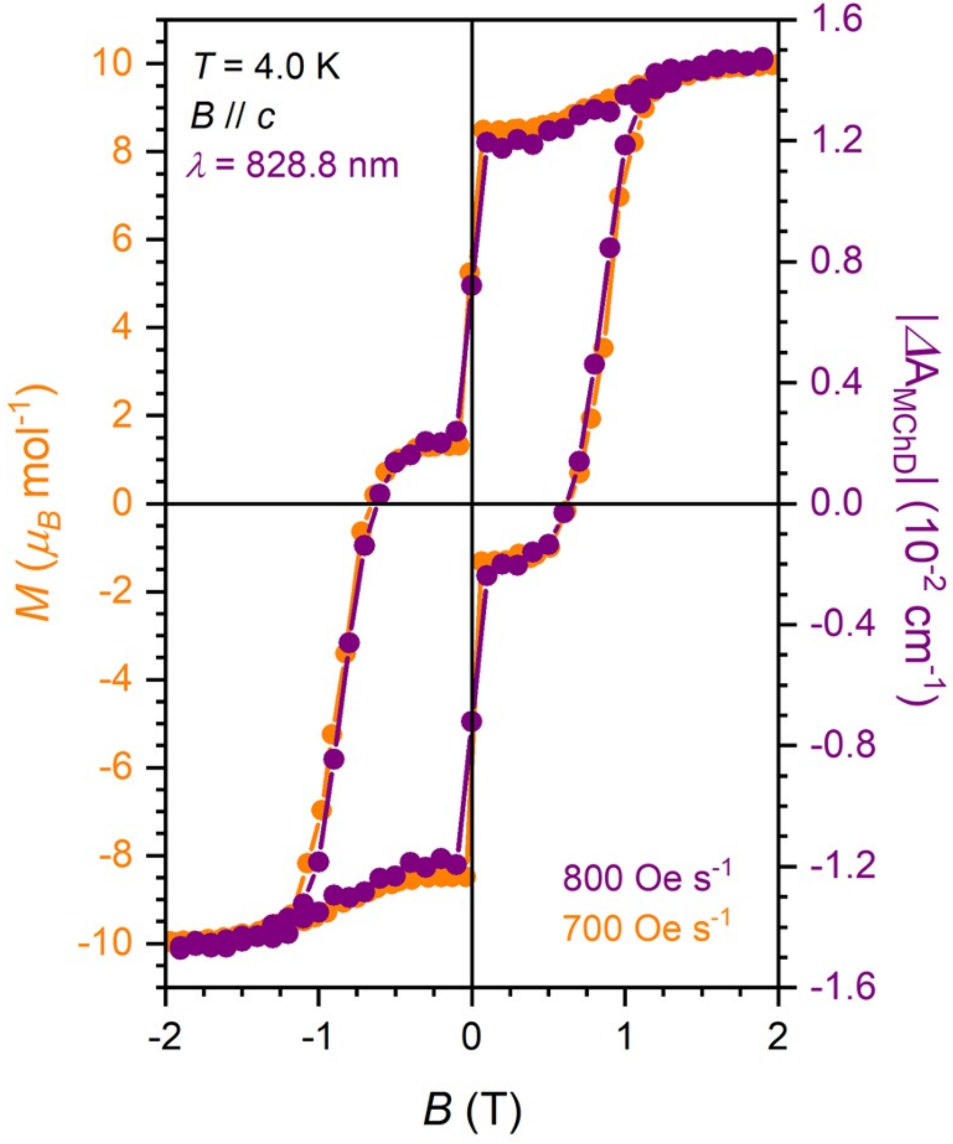
Optical detection of Magnetic Hysteresis



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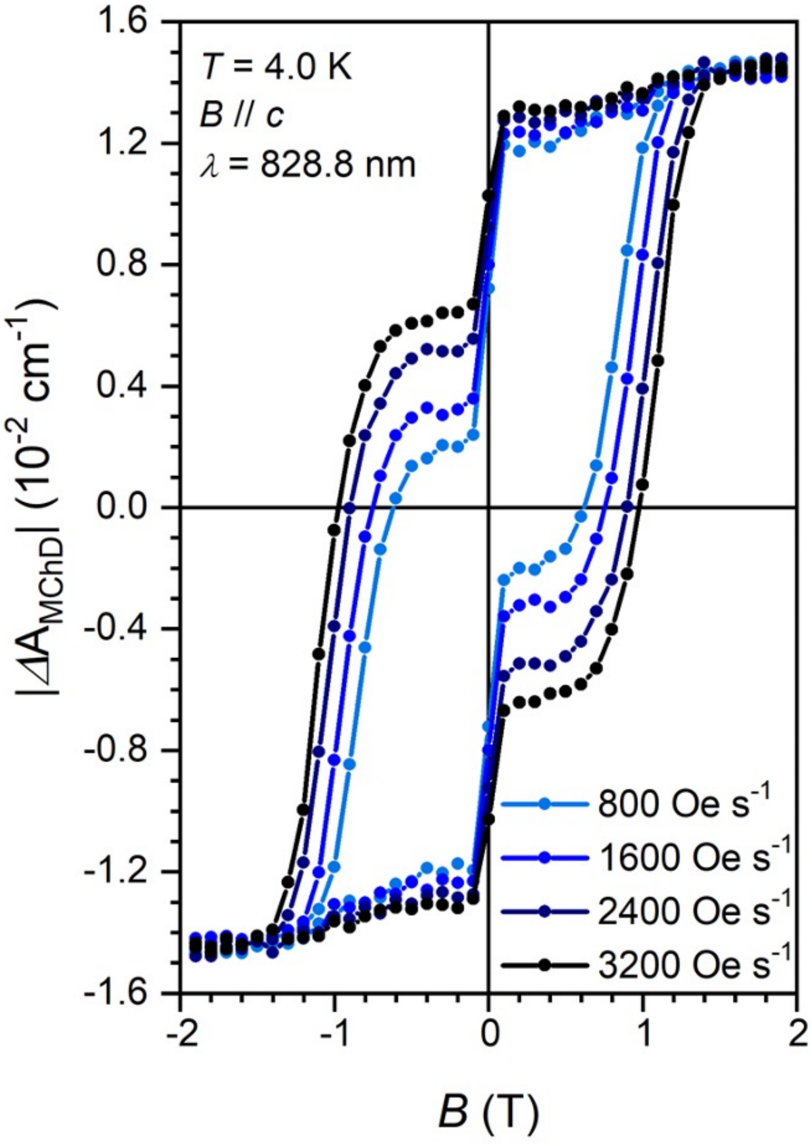
Optical detection of Magnetic Hysteresis



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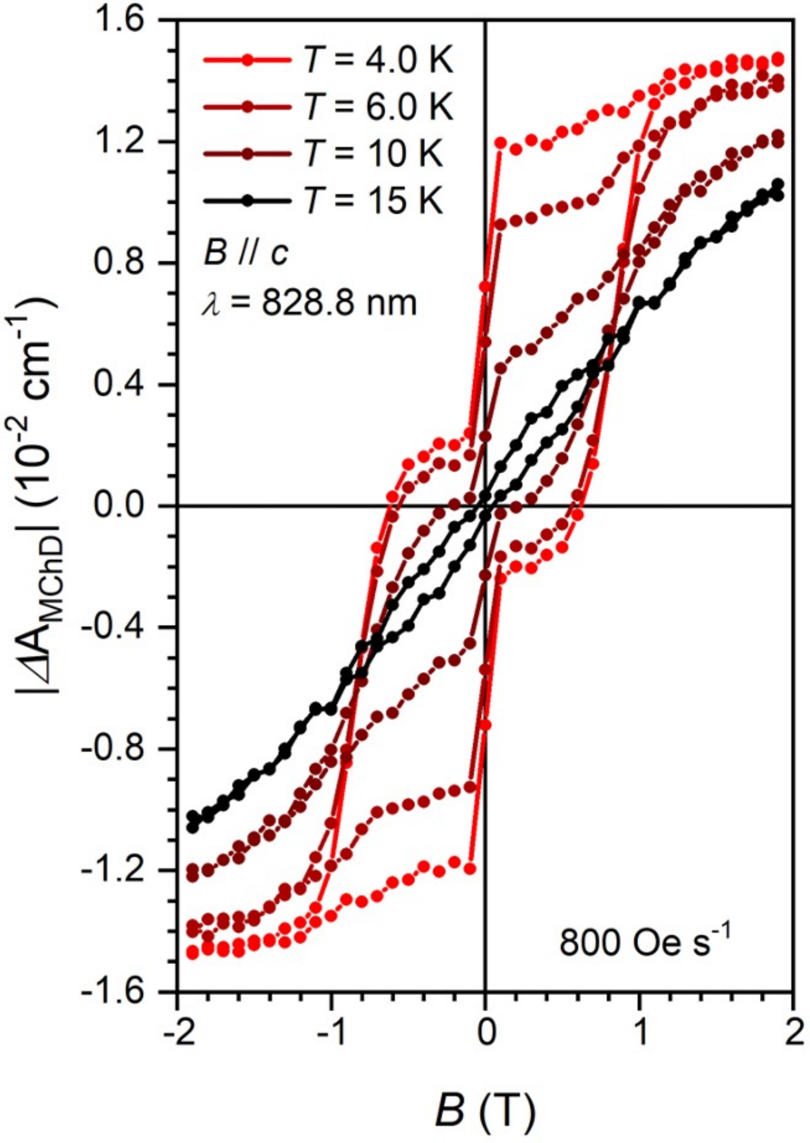

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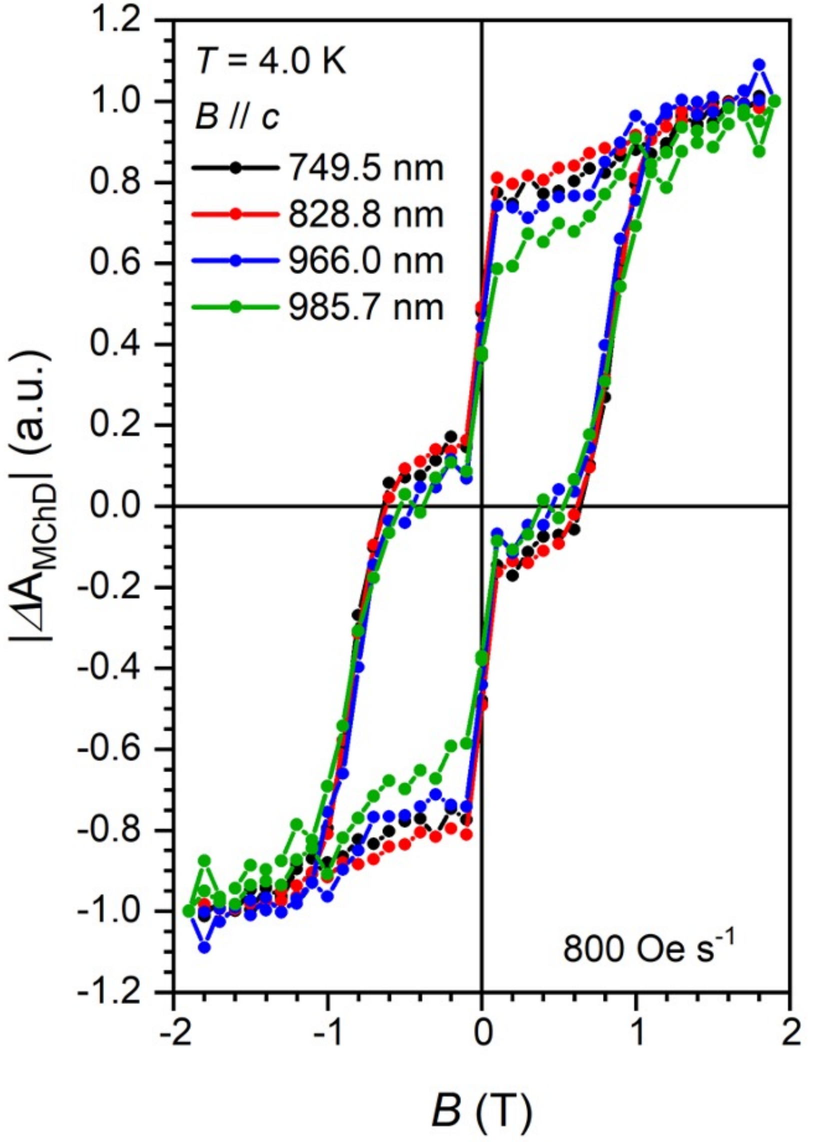
Optical detection of Magnetic Hysteresis



J. Am. Chem. Soc. **2024**, 146, 23624

Conclusions

- ✓ **Magneto-Chiral Effects** are fascinating phenomena shown by **chiral molecules and materials** driven by symmetry arguments

- ✓ **MChD** is an intriguing **manifestation of light-matter interaction** of chiral magnetic systems **independent of the polarization state of light** and **proportional to the magnetization**

- ✓ **A rational chemical approach** can reveal the **microscopic parameter** that governs MChD **to enhance MChD signals intensity** and their observable temperatures **up to room temperature**

- ✓ **MChD can be used to optically readout magnetic memories without need of light polarization using visible light**

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- ✓ **PRINCIPE**
- ✓ **MaChiNaCo**
- ✓ **SWITCH-MChD**

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EMFL European Magnetic Field Laboratory