Institut de Physique et Chimie des Matériaux de Strasbourg

« Nouveaux » composés magnétiques, (supra)conducteurs et multifonctionnels: l'approche composite et hybride

Pierre Rabu

IPCMS UMR7504 (CNRS-ULP-ECPM),
23, rue du Loess, F67034 Strasbourg, France;
pierre.rabu@ipcms.u-strasbg.fr

INTRODUCTION

(Multi)functional/ Adaptable Materials

Bulk extended systems

Magnets, Supraconductors, Spin polarized, Multiferroic … ($LaMnO_3$, $(La,Sr)CoO_3$, $BiFeO_3$, MOFs …)
Photo-magnetism ($CsMn[Cr(CN)_6].H_2O$, …)
Photovoltaics (Si, ZnO, TiO_2…)

Integration / quantum effects

Complex heterostructures
Thin film multilayers (metal/oxide/organic semi conductor, Nanoparticles, molecules, ….)

Hybrid systems

OUTLINE

INTRODUCTION

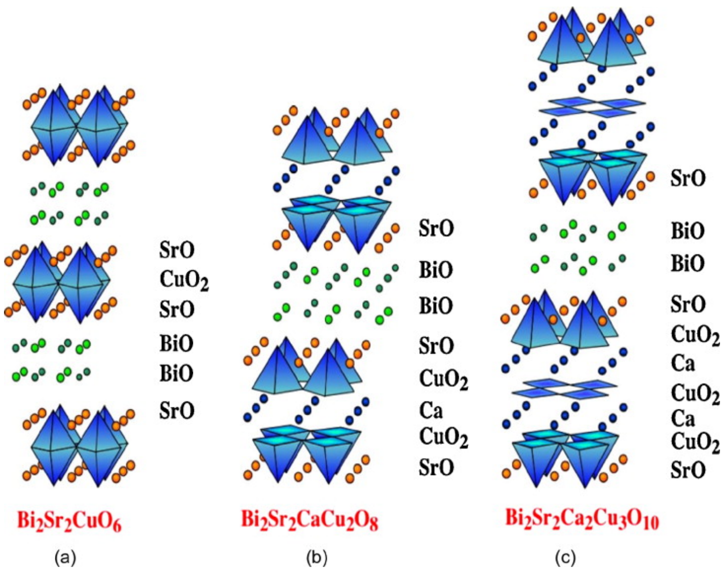
Molecules
Extended Solids
Nano-composites

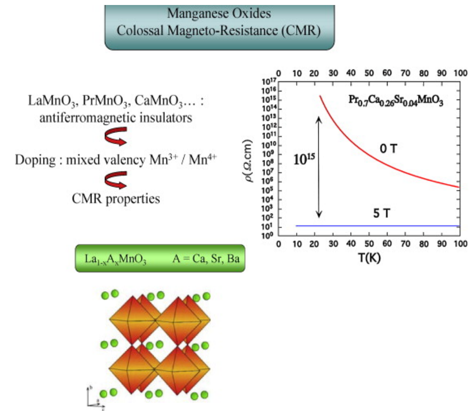
Interaction mechanisms and tuning of the magnetic properties
(structure, topology, dimensionnality, anisotropy)

Toward Multiproperties & Multi-ics

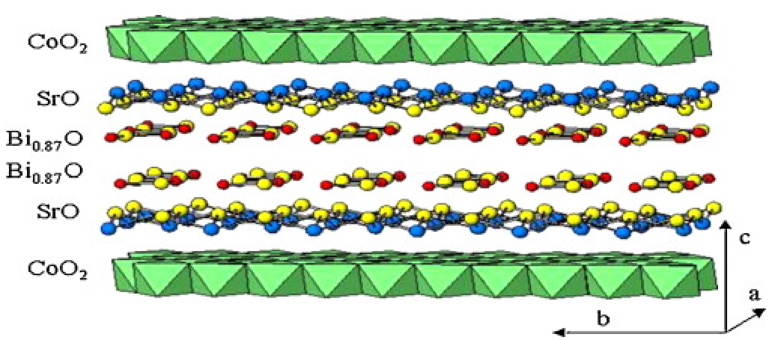
Conclusion

Oxydes, ...

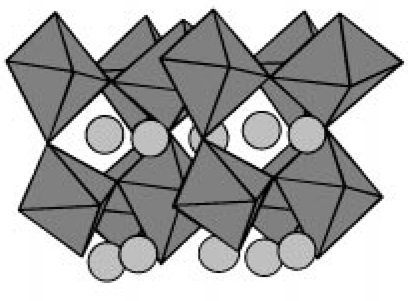




misfit cobaltite (Bi0.87SrO2)2 (CoO2)1.82



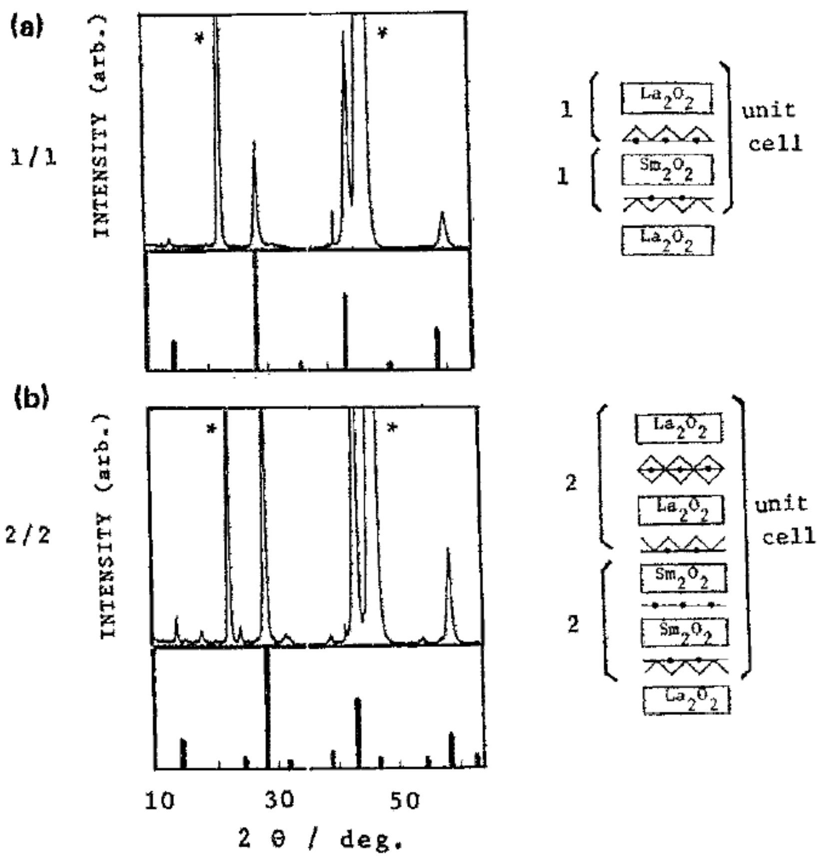
B. Raveau, Comptes Rendus Chimie 14, Issue 9, 2011, Pages 856–864

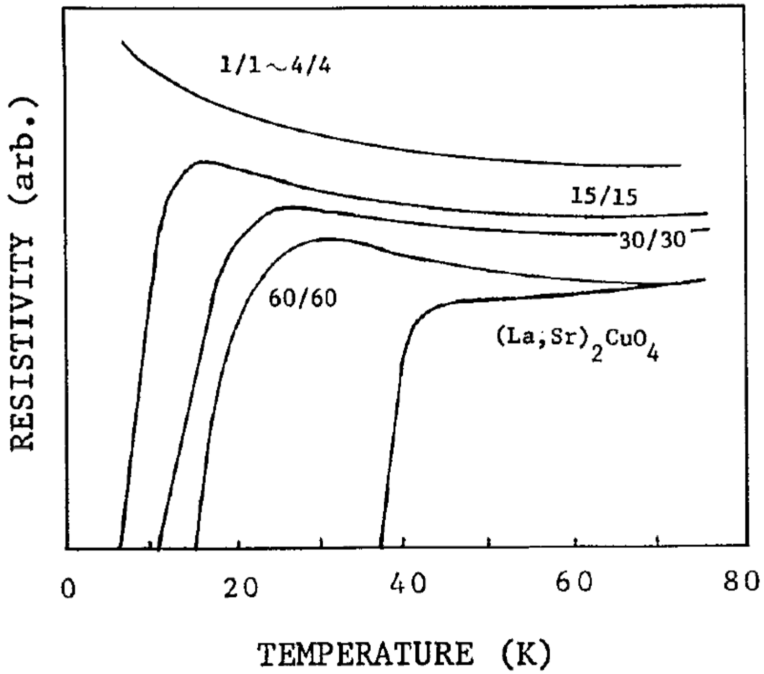


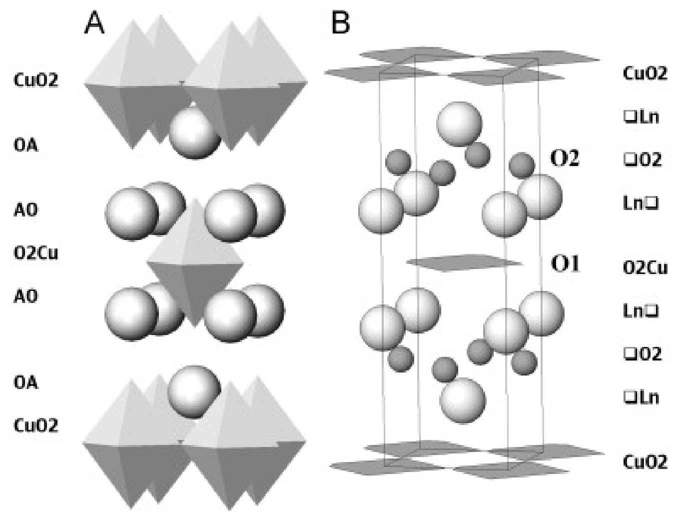
BiMnO3
T. Atou, et al.
J. Solid State Chem. 145, 639}642 (1999)

• • •

Reconstruction par voies physiques







(La,Sr)2CuO4/Sm2CuO4
superlattices prepared by excimer laser deposition
Hitoshi Tabata, Tomoji Kawai, and Shichio Kawai
Appl. Phys. Lett. 58, 1443 (1991)

Superconductivity and magnetic field induced spin density waves in the (TMTTF)2X family

Journal de Physique I (1994), 4, (10), 1539-49.

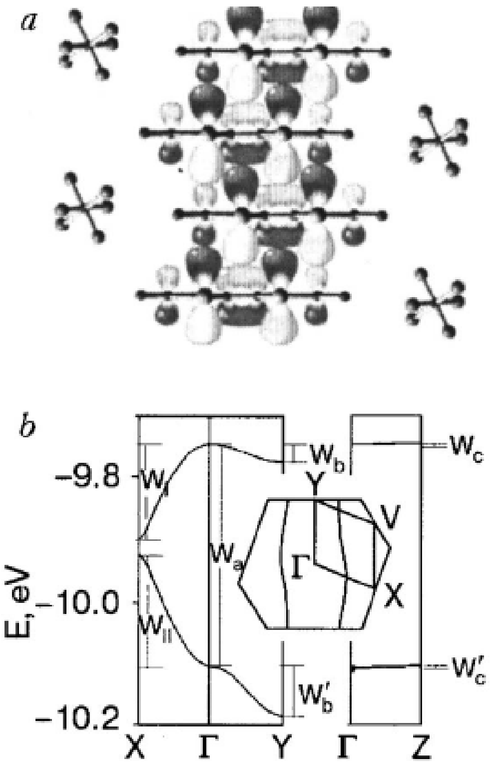


FIG. 1. A side view of the Bechgaard/Fabre salt crystal structure with the electron orbitals of the organic stacks (courtesy of J. Ch. Ricquier) (*a*). Electronic dispersion relation and projected 2D Fermi surface of $(TMTTF)_2Br$ (reprinted with permission from Ref. 13. Copyright 1994 by EDP Sciences) (*b*).

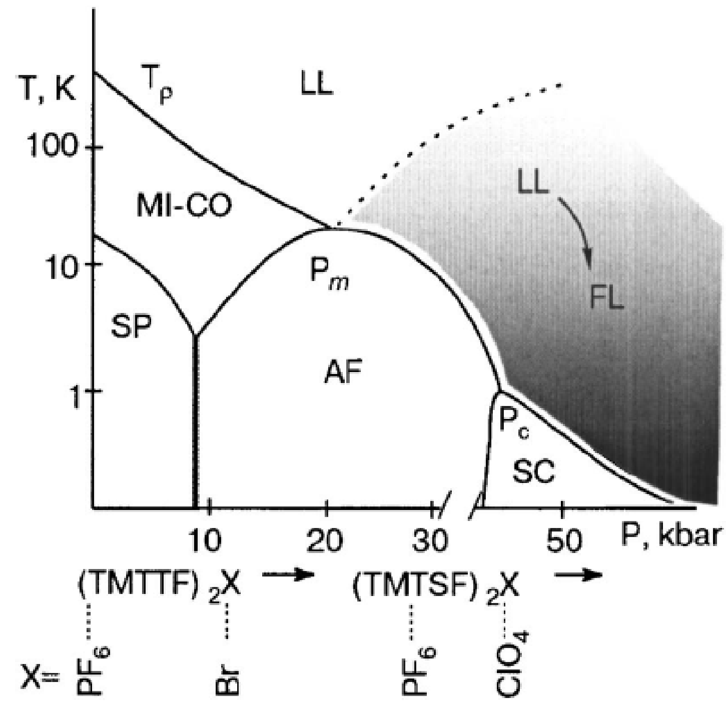
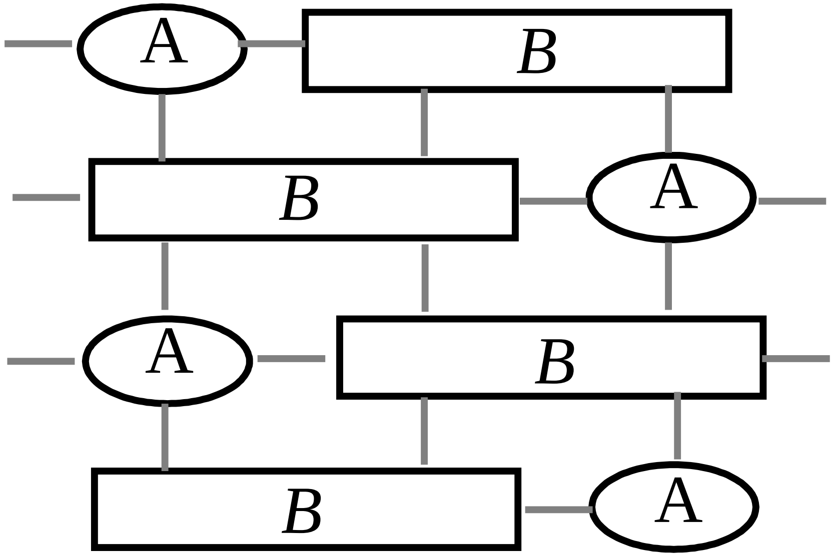


FIG. 2. The generic phase diagram of the Bechgaard/Fabre salts as a function of pressure or anion X substitution; Luttinger liquid (LL), Mott insulator (MI), charge order (CO), spin-Peierls (SP), antiferromagnetism (AF), superconductivity (SC), Fermi liquid (FL).

Structure - Property in the solid (Magnetism, chirality, luminescence...)

- Control :
- Elementary bricks, Topology, Interaction

- Approaches:
- Bulk vs Bottom-up



O/I Hybrid Materials :

Multiproperty Toward synergy

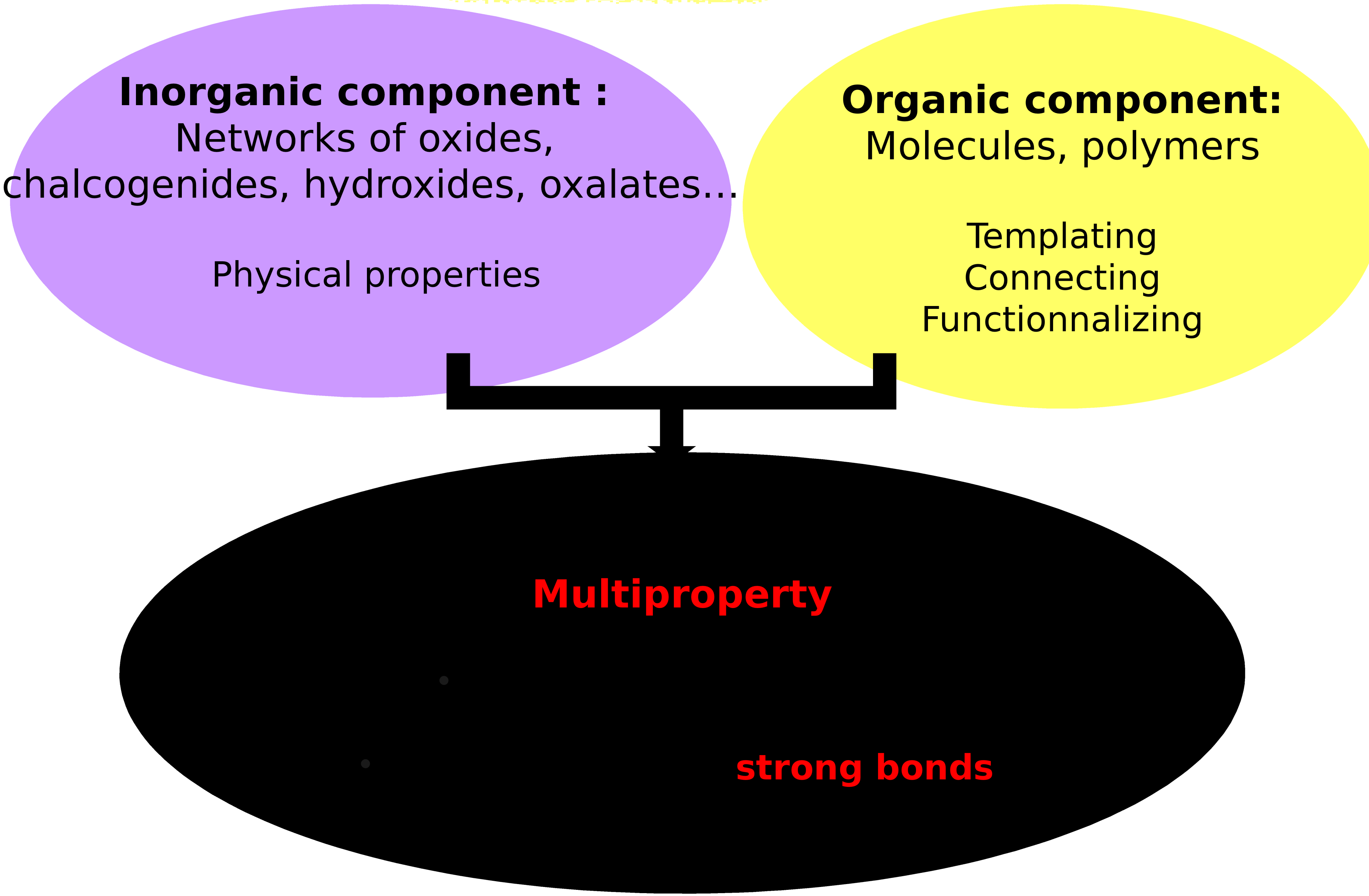
INTRODUCTION

To synthesize organized magnetic and multifunctional multilayers

by design

utilizing low-temperature chemical routes

Hybrid Organic/Inorganic Materials



Concepts and issues

Combining Organic and inorganic building blocks

Cooperativity inside the inorganic network

Flexibility of the organic entity (but needs to devellop chemistry)
bringing either luminescence, chirality, (photo)magnetism, photochromism, ...

Synergy ?
Chemical bond: van der Waals to covalent
Intercalation, grafting
Which interaction between 2 electronic populations ?

Stratégies de synthèse

chimie du solide, chimie de coordination, chimie organique, …

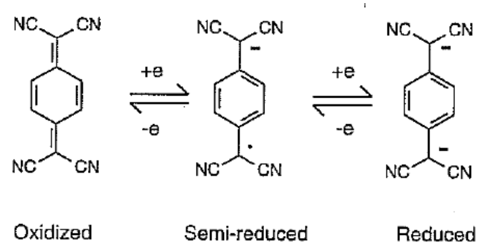
1) briques connues: polymères préformés, systèmes lamellaires, solides minéraux poreux, verre, particules de métaux ou d'oxydes...

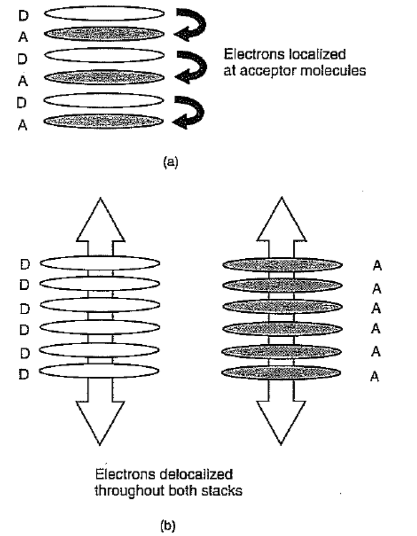
2) Vers une approche moléculaire: les propriétés résultent d'interactions intermoléculaires spécifiques.

3) contrôle des processus d'auto-assemblage des entités « moléculaires » de départ,
bibliothèque de précurseurs,
structuration, la stabilité et propriété physique désirées.

CTC conducteurs

Processus redox

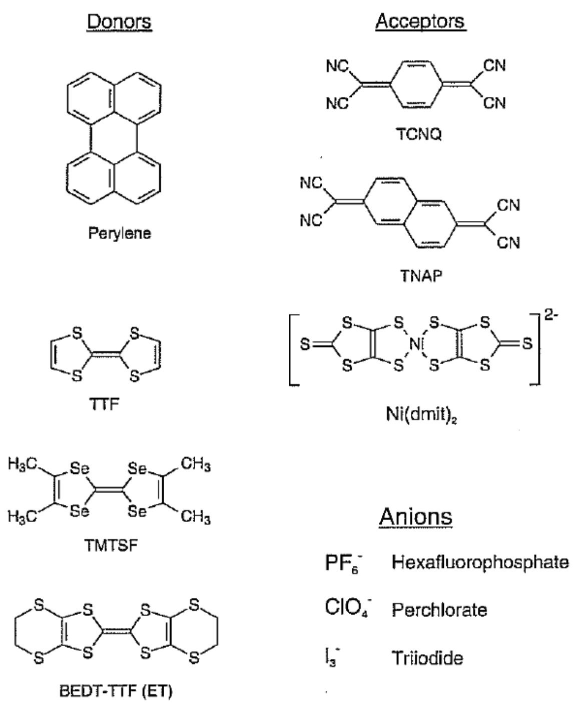


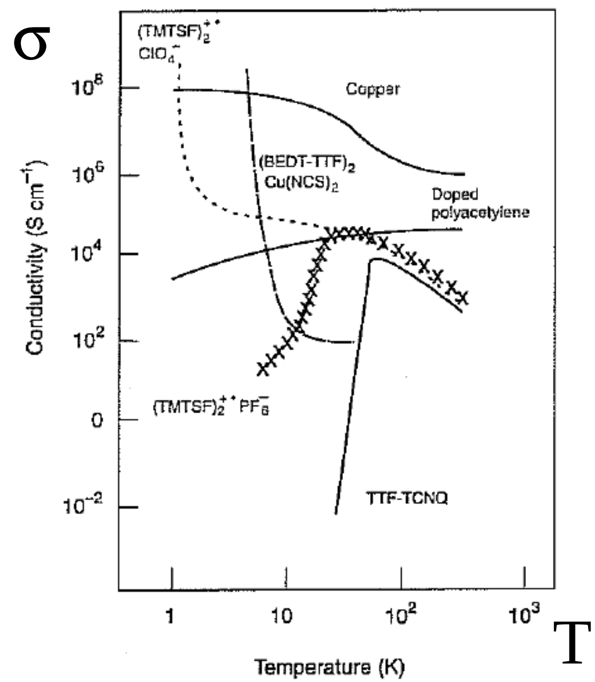


nature chimique des composants

transfert de charge, ρ: D+ρA−ρ

structure cristalline





Molecular hybrids

indirect coupling J between localized spins (d electrons) via conduction electrons material (π-electrons) formed by organic donors and inorganic magnetic complexes

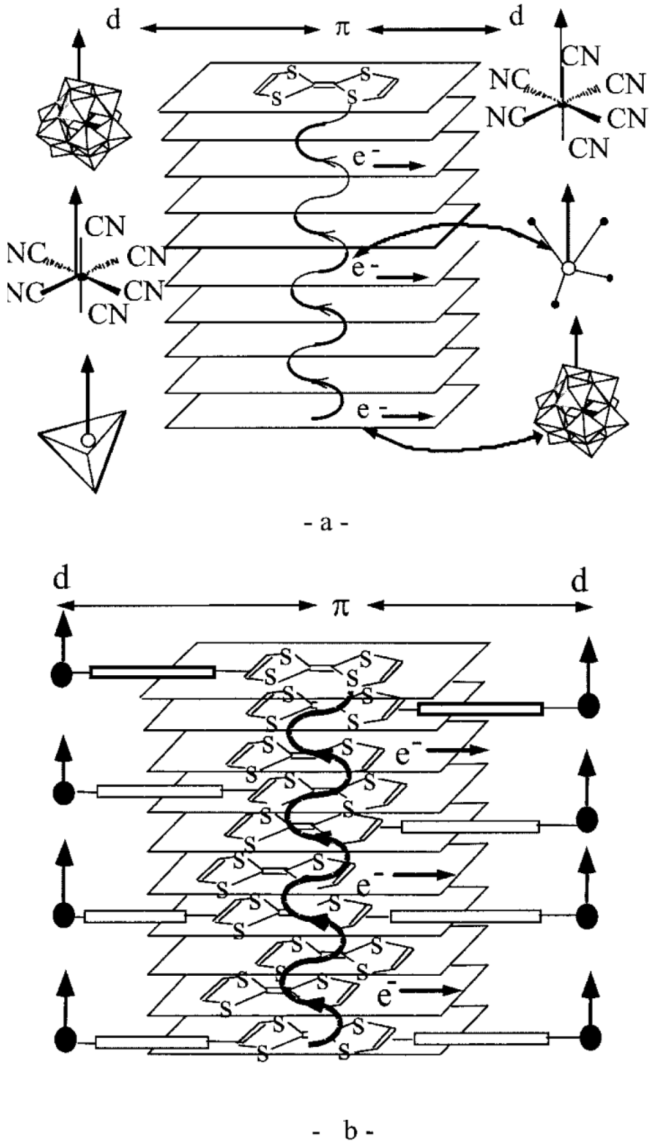
Ex. conducting magnets

p-d systems

flexibility

Richesse chimique

Liaisons O/I faibles



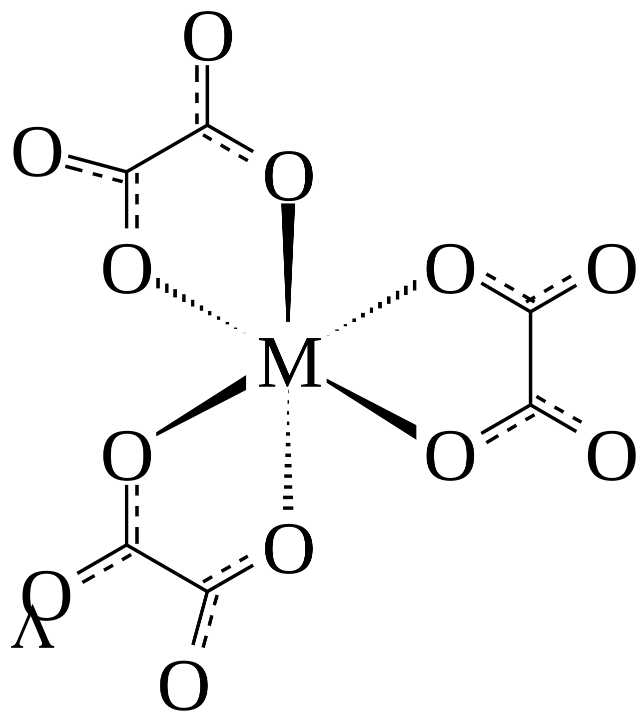
ıe 1. Representation of the indirect exchange mechanism; (a) gh space interaction, (b) through bridge interaction

L. Ouahab, T. Enoki, ejic 2004 933

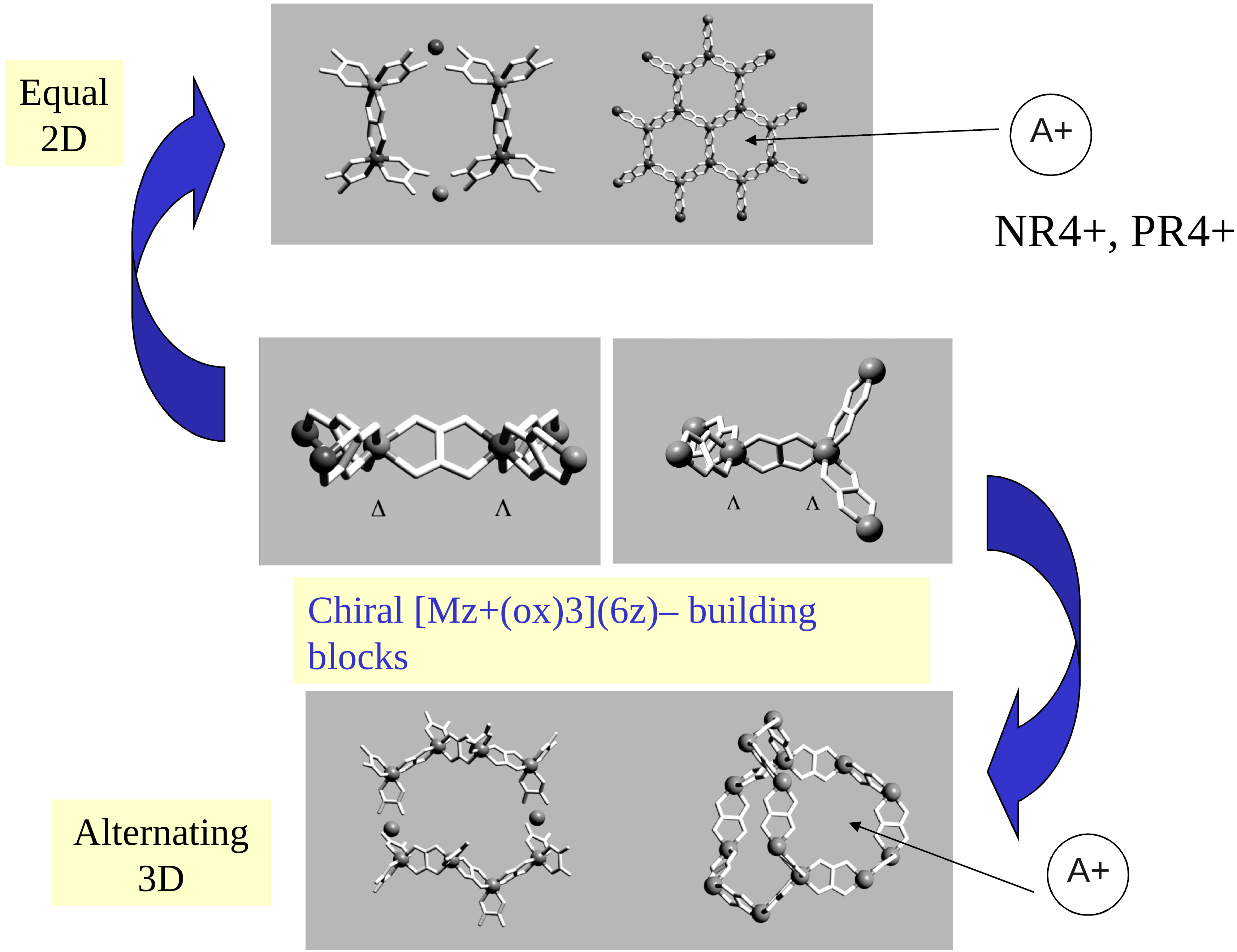
SOUS-RESEAU INORGANIQUE ETENDU (2D/3D)

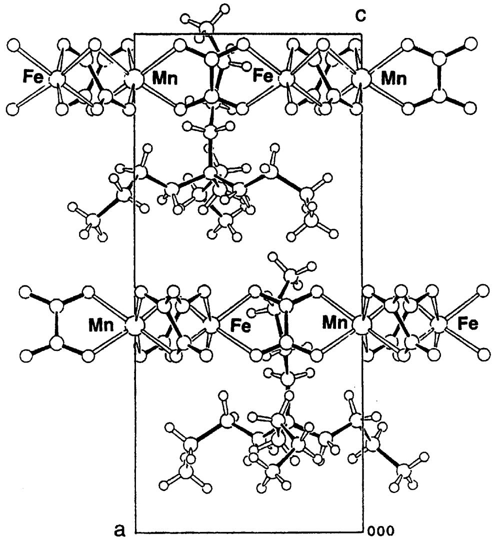
Oxalates mixtes (2D/3D)

$[A^+][MM'(C_2O_4)_3]^-$



Chiral $[M^{z+}(ox)_3]^{(6z)-}$ building blocks


Equal
2D
A+
NR4+, PR4+
Δ
Λ
Λ
Λ
Chiral [Mz+(ox)3](6z)– building blocks
Alternating
3D
A+



[N(Bu)4][MnIIFeIII(ox)3], *P*63

d inter-feuillets: 8.9 – 10.2 Å

Une grande variété de comportements
(F, FI, AF, AFCanté)
f(MII /CrIII, A+)

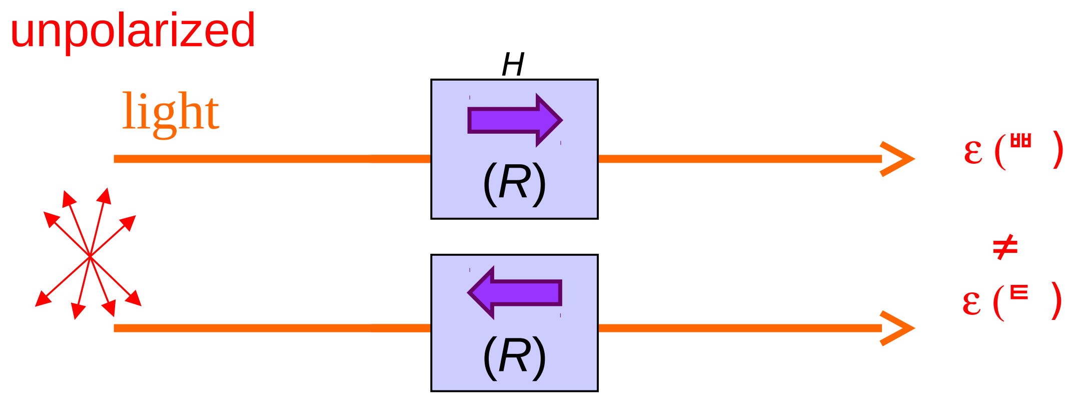
MII /CrIII

[N(Bu)4][MIIMIII(ox)3]

	MnII S=5/2	FeII S=2	CoII S=3/2	NiII S=1	CuII S=1/2	
CrIII S=3/2	←		F		→	TC < 14 K
FeIII S=5/2	AF ↓ ≠ A+ AFC	FI 43 K		FI 28 K		

Chiral magnets

Absorption coeff. $\boldsymbol{\varepsilon}(\mathbf{k},\mathbf{M})=\varepsilon 0+\alpha \mathrm{NCD}\,\mathbf{k}+\beta \mathrm{MCD}\,\mathbf{M}+\gamma \mathrm{MChD}\,\mathbf{k}\cdot\mathbf{M}$



Second order effect

crossing effect between natural circular dichroïsm and magnetic circular dichroïsm

G.H. Wagnière, A. Meier, *Chem. Phys. Lett.* 93, **1982**, 78
G. L. J. A. Rikken, E. Raupach, *Nature*, **1997**, *390*, 493

CHIRAL MAGNET and MAGNETO-CHIRAL EFFECT

Wagnière, Meier, **1982**; Rikken, Raupach **1997**

Train et al. Nature Materials 7, **2008**, 729

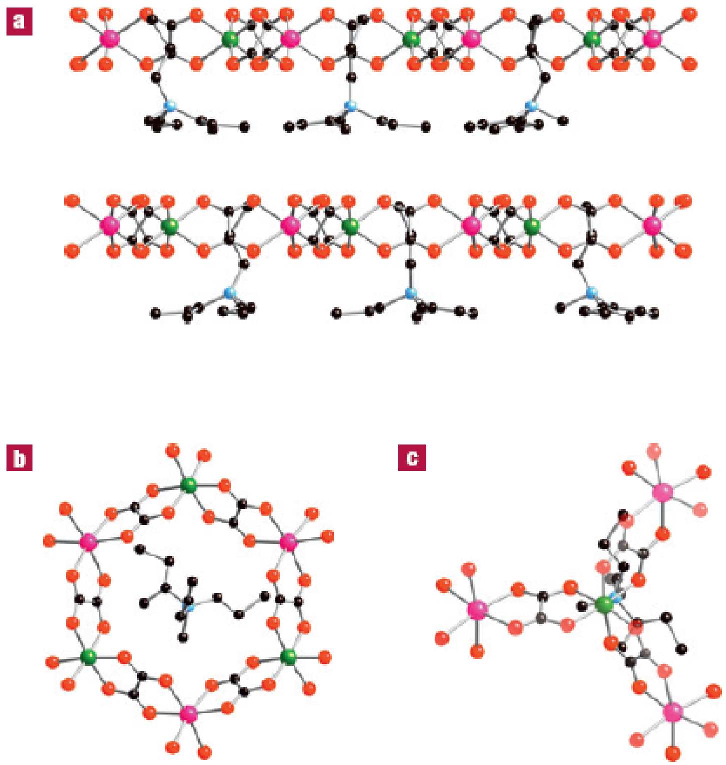


Figure 3 Crystal structure of 1. a–c, Views along the [010] (**a**), the [001] (**b**) and slightly offset [00$\bar{1}$] (**c**) directions. The alkyl chains are represented in one of their possible positions.

[(*D*)-Mn(*L*)-Cr(C2O4)3-][N(CH3)(*n*-C3H7)2((*S*)-*s*-C4H9+]

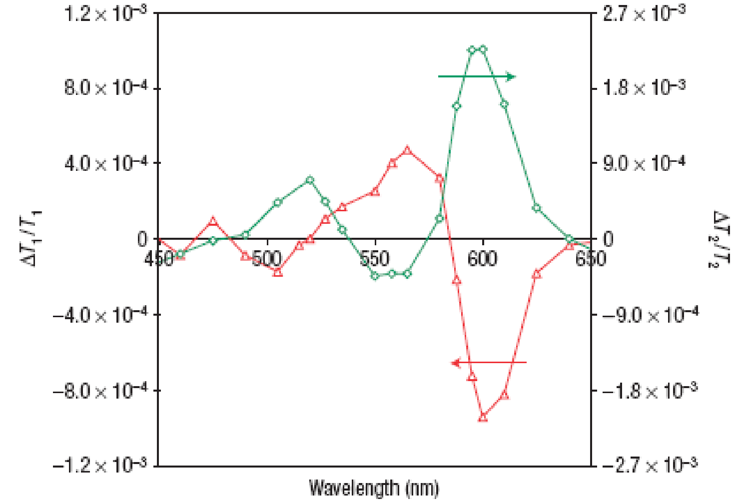


Figure 5 Inversion of the magneto-chiral dichroism with the enantiomer.

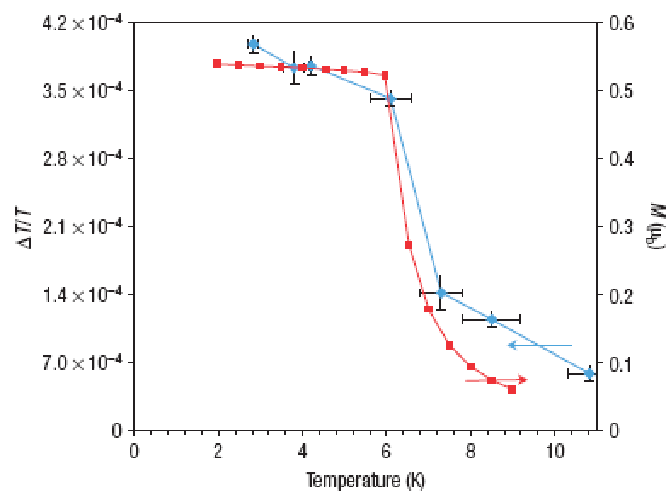
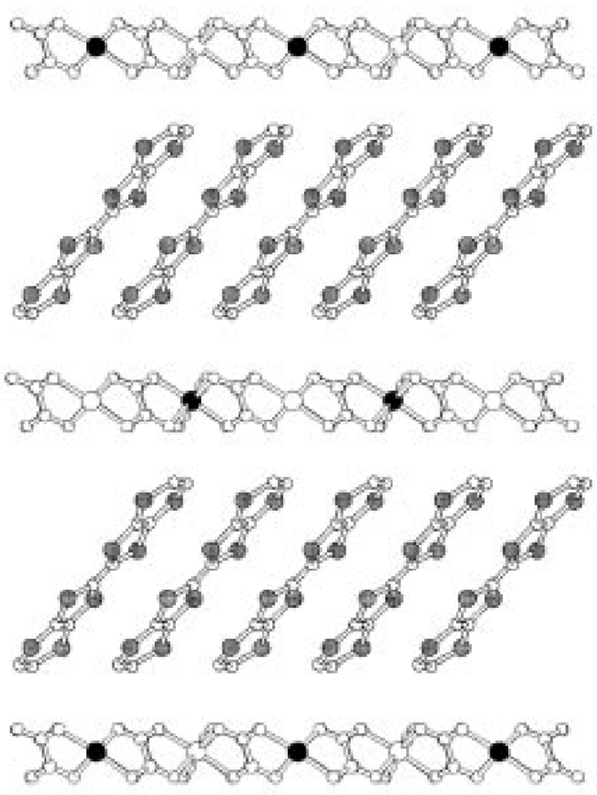


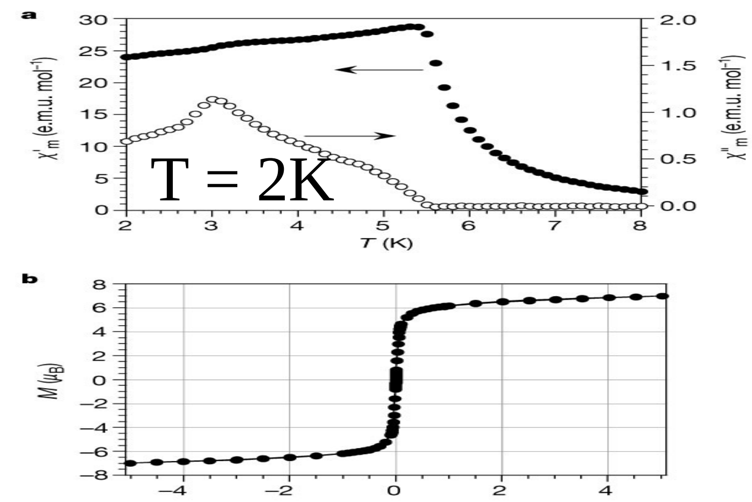
Figure 6 Enhancement of magneto-chiral dichroism at the Curie temperature of

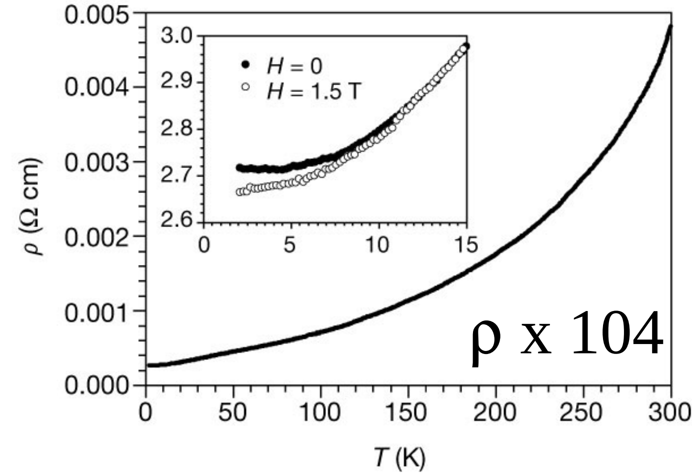
COMPOSES MULTIPROPRIETES

$[MnCr(C_2O_4)_3^-][A^+]$

BEDT-TTF



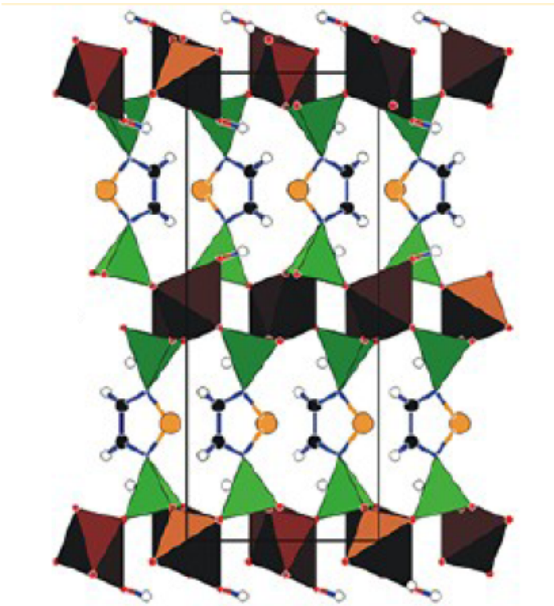




Coronado et al.
Nature (2000), 408(6811), 447-449

magnétisme (TC = 5.5 K
+ conductivité (σ_{RT} ~250 S cm^{-1})

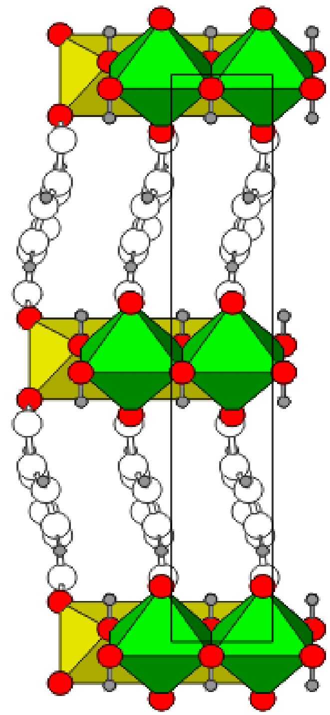
Plus de synergie?



4

$Mn_2(O_3P\text{-}C_4H_2S\text{-}PO_3).2H_2O$

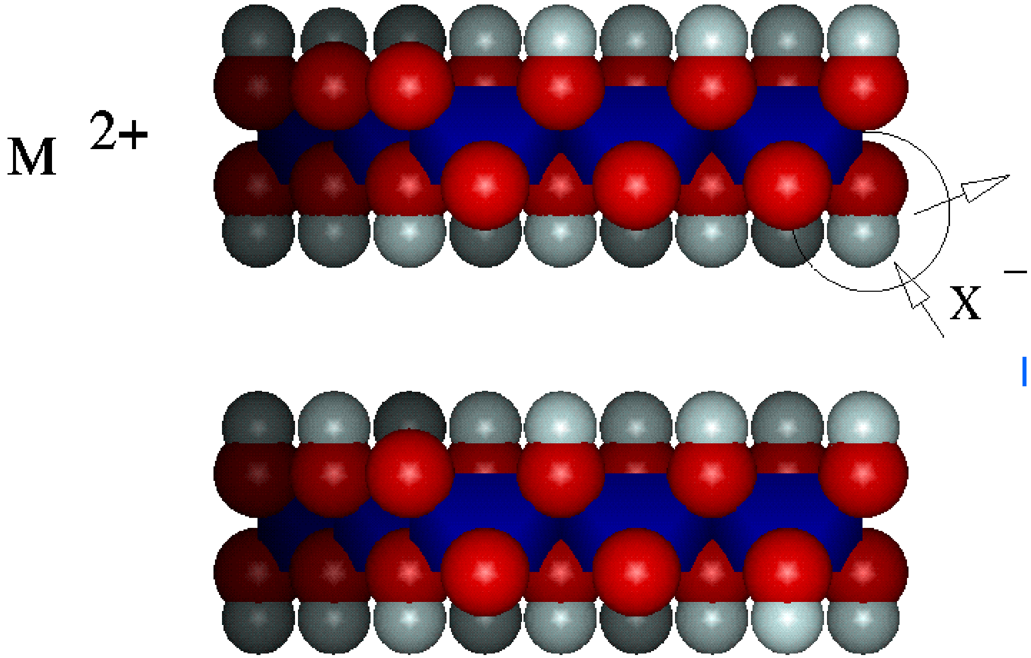
Jean-Michel Rueff et al.,
Inorg. Chem., 2012, 51 (19), pp 10251–10261

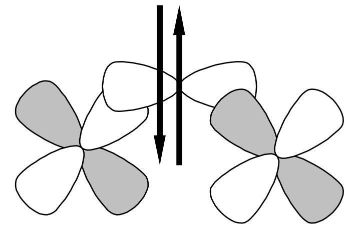


Co2(OH)2(TP)

Chem. Mater. 12, 2805-2812 (2000)
Solid State Sciences, 5, 321-326 (2003)

Hydroxide based organic -inorganic magnets





In plane Magnetic exchange coupling

$M(OH)_2$

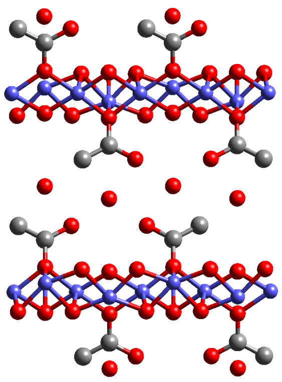
2D triangulaire

Mn, Co, Ni, Cu

Synthesis (1)

2 Cu(CH3COO)2 + 3 NaOH

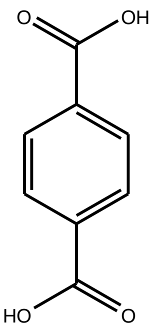
60 °C in water



+ sodium acetate

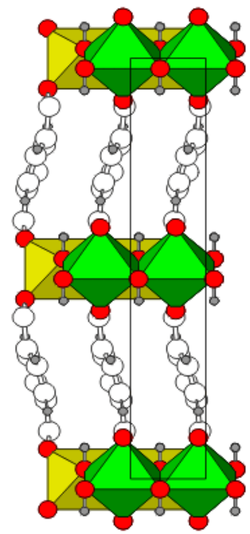
Cu2(OH)3(CH3COO).H2O

2 CoCl2 + 8 KOH + 3



H2O (solvothermal)

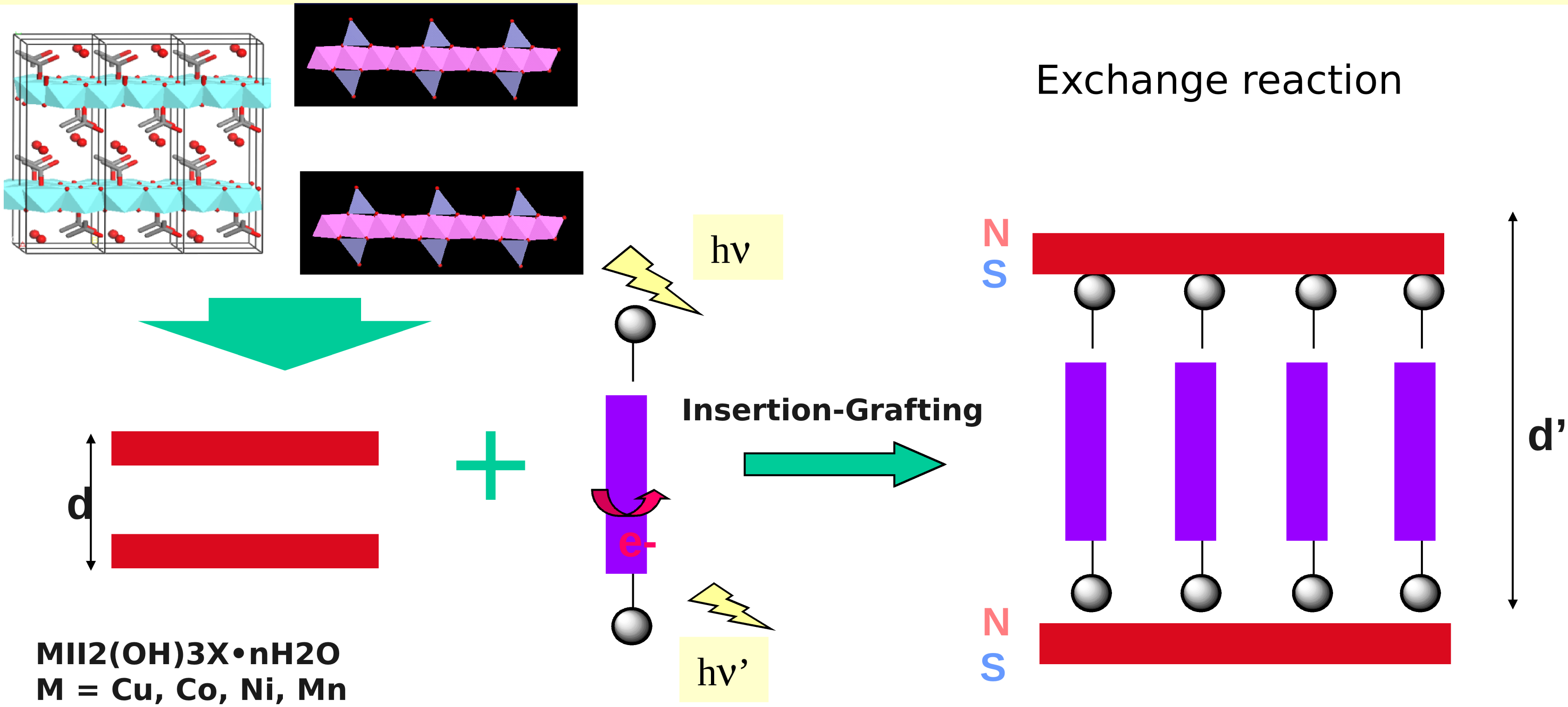
220 °C
64 hrs



Co2(OH)2(Tp)

Valérie Laget, PhD Thesis, Strasbourg
Aude Demessence, PhD Thesis, Strasbourg 2006

Synthesis (2)



MII2(OH)3X•nH2O
M = Cu, Co, Ni, Mn
X = OH-, NO3-,
CH3CO2-

d < 10 Å:
AF 3D

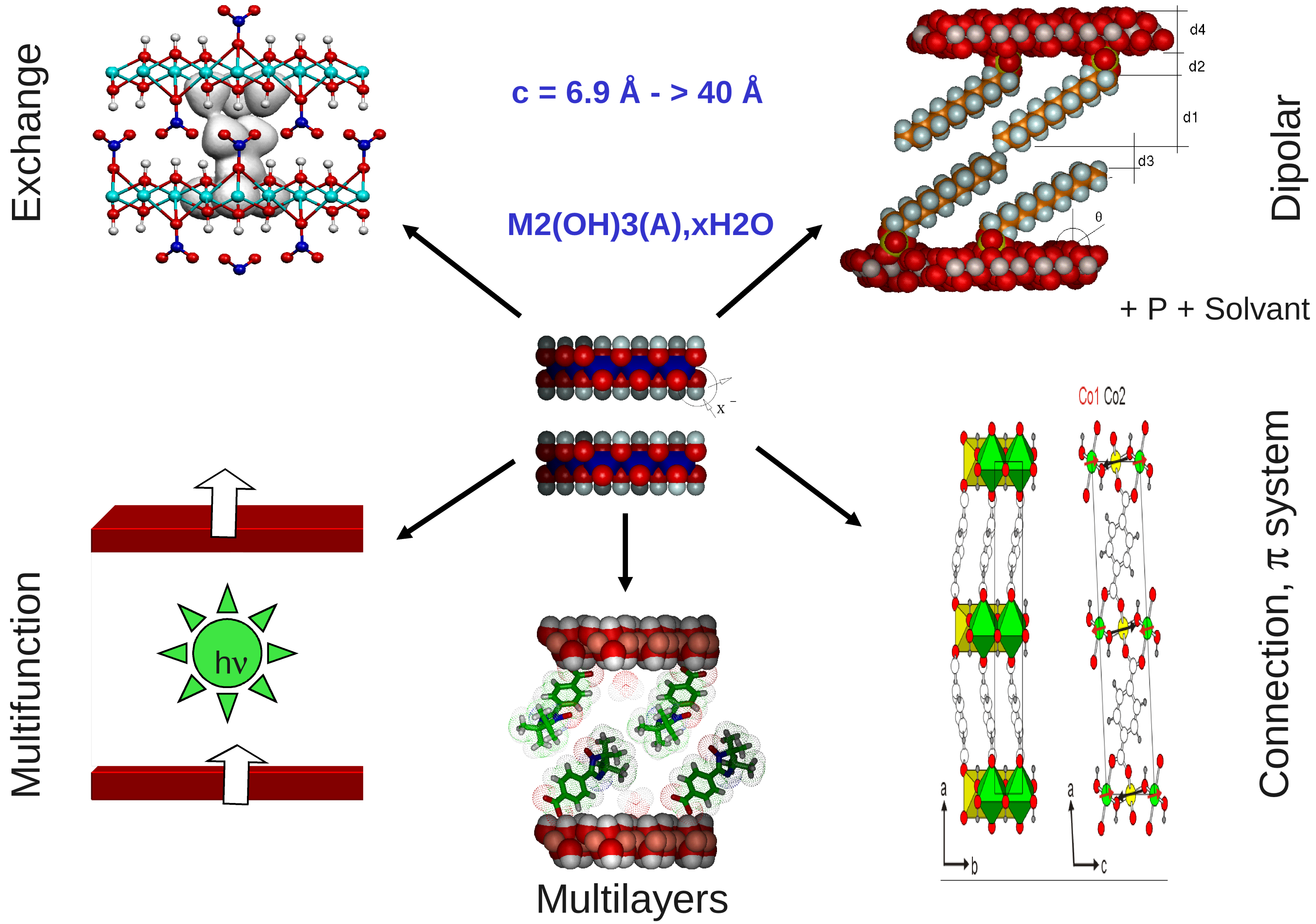
Anchoring function COO-, SO3-…

d > 10 Å:
F 3D (dipolar)

luminescent or chiral molecule

Valérie Laget, PhD Thesis, Strasbourg 1999
Aude Demessence, PhD Thesis, Strasbourg 2006

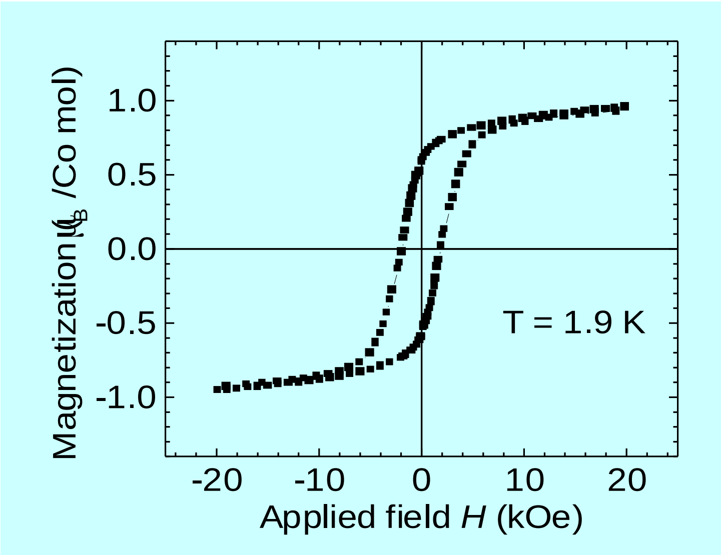
Controlling properties by assembling hybrid organic – inorganic networks

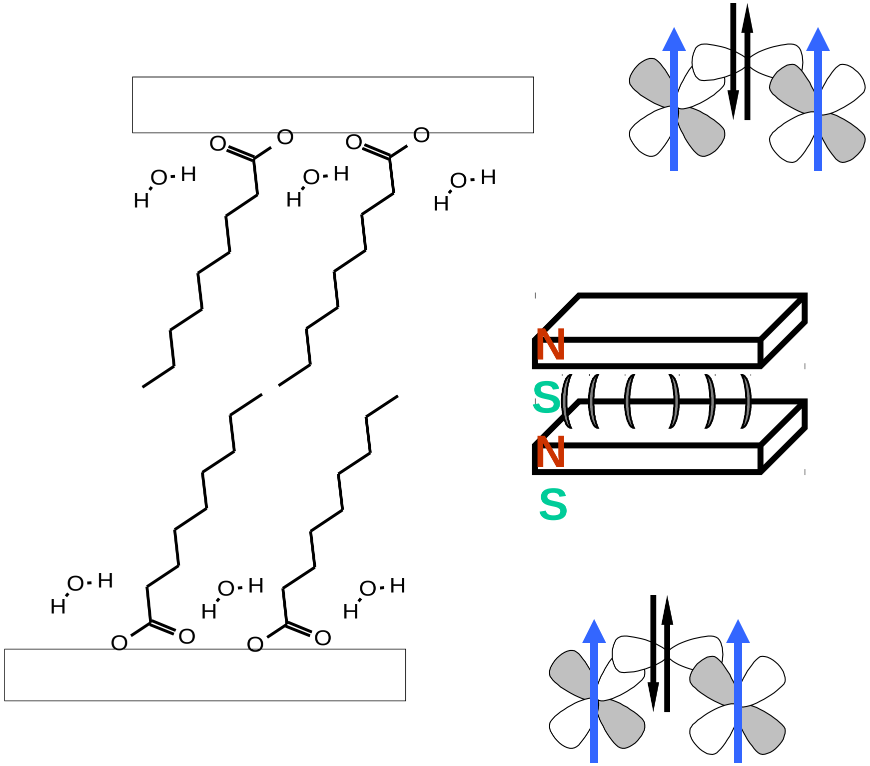


Adv. Eng. Mater. 5(4) 2003; *Chem. Mater.* 16 2004; *Chem. Mater.* 18 2006; *J. Mater. Chem.* 19 2009; *J. Mater. Chem.* 20 2010; *Dalton Trans*. 39 2010; *Chem. Soc. Rev*. 40 (2) 2011

mécanismes d'interaction magnétiques

M2(OH)3(NO3)2(s) + HX + KOH → M2(OH)3(X).zH2O(s)+ K NO3(aq)



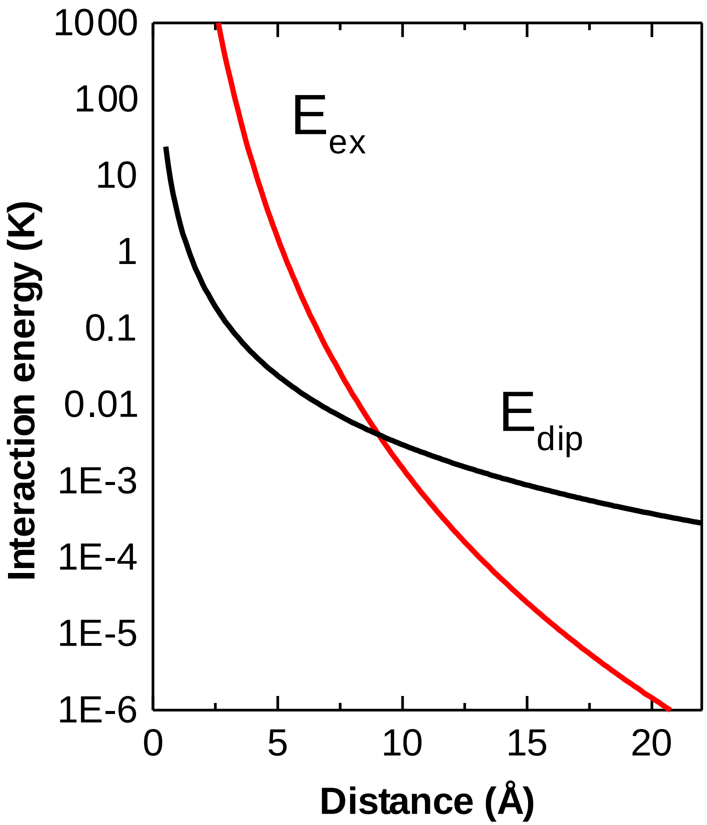


Co2(OH)3(C12H25OSO3)•2H2O
d 001 = 25.4 Å

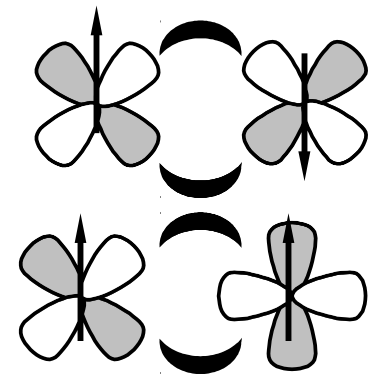
Inter-plane Interaction : dipolar
Scaling theory : 3D LRO

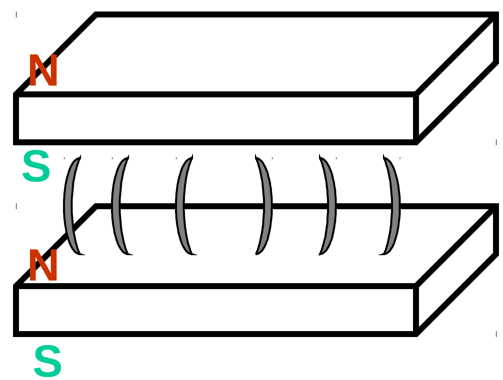
V. Laget, et al J. Mater. Chem., 9 (1999). .
M. Drillon, P. Panissod, P. Rabu, J. Souletie, V Ksenovontov, P. Gütlich Phys. Rev. B 65, (2002).

Inter-plane Interaction
Dipolar versus Exchange Interaction



$E_{ex} \propto d^{-10}$





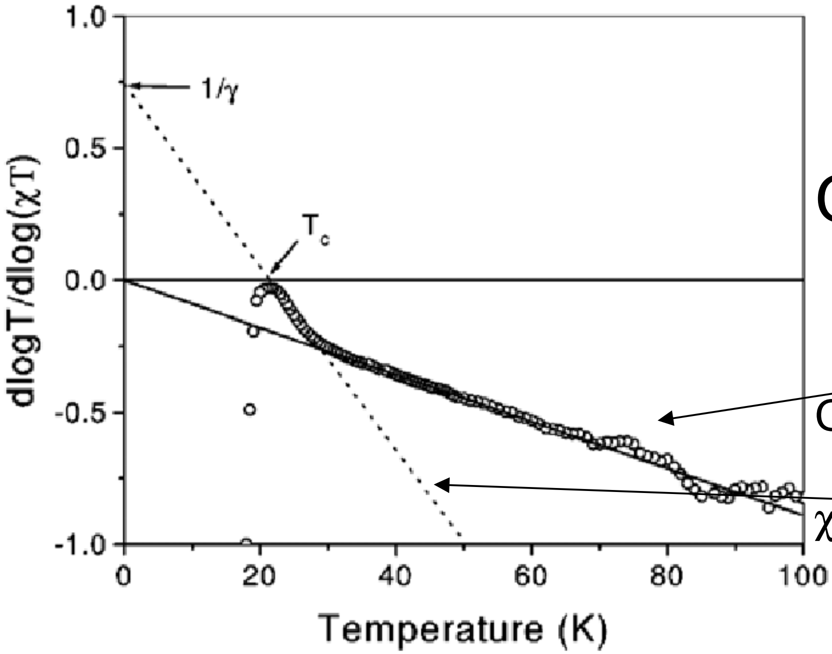
$E_{dip} \propto m^2 . d^{-\nu}$ ($\nu \leq 3$)

$$H_{dip} = \mu_i \mu_j / r_{ij}^3 - 3 (\mu_i \; r_{ij})(\mu_j \; r_{ij}) / r_{ij}^5 \approx \propto 1/ r_{ij}^3$$

V. Laget, C. Hornick, P. Rabu, M. Drillon, R. Ziessel Coord. Chem. Rev., 178-180 (1998)
M. Drillon, P. Panissod, J. Mag. Mag. Mat., 188 (1998)

Magnetic Dimensionality
2D - 3D

spin correlation length $\xi = \xi 0(1\text{-}Tc/T)\text{-}\gamma$,
$\chi T = C\ (1\text{-}Tc/T)\text{-}\gamma = C(1\text{-}Tc/T)\text{-}\theta/Tc$ with $\theta = \gamma Tc$ ⟶ $d\ln T/d\ln(\chi T) = -\ (T\text{-}Tc)/\gamma Tc$
C = Curie constant.



Cu2(OH)3(n-C10H21CO2)

C2exp(βJ/*k*T), 2D Heisenberg

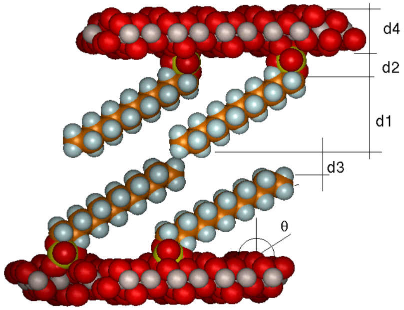
$\chi T = 0.40(1\text{-}21.05/T)\text{-}1.36$

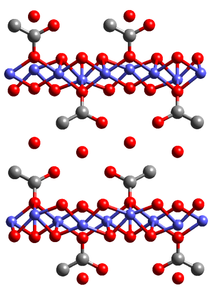
''crossover'' à TC =21.05 K
γ=1.36 Ordre ferromagnétique 3D
(γ=1.24 for Ising, 1.32 for XY, and 1.385 for Heisenberg spins)

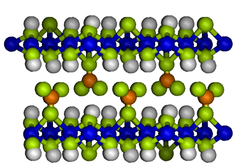
V. Laget, et al J. Mater. Chem., 9 (1999). .
M. Drillon, P. Panissod, P. Rabu, **J. Souletie**, V Ksenovontov, P. Gütlich Phys. Rev. B 65, (2002).

Chemical Pressure Effect

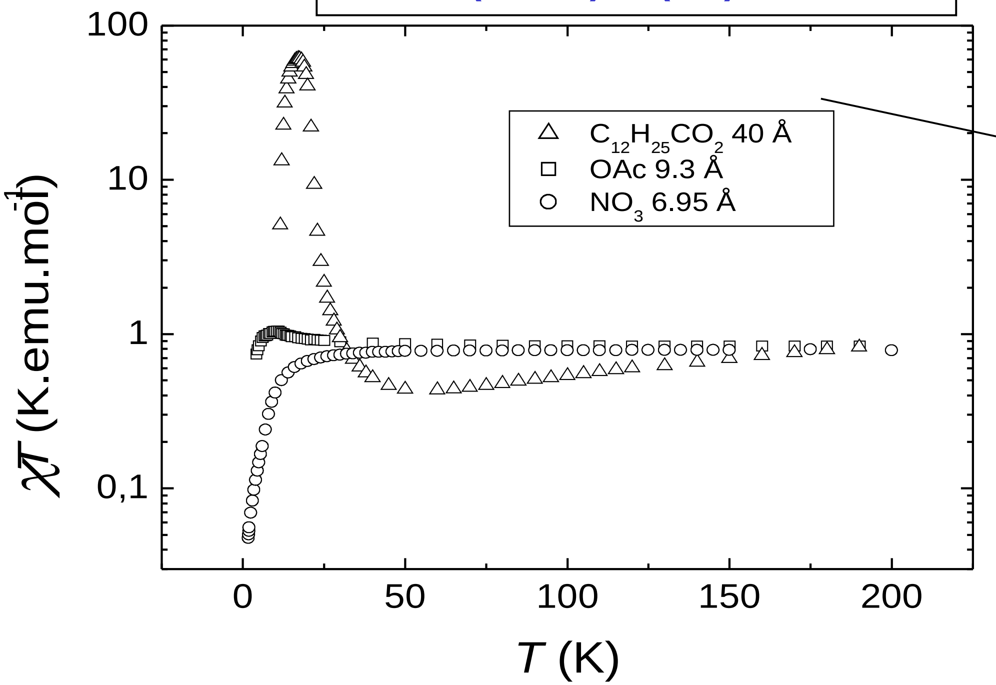
Copper(II) hydroxy n-alkylcarboxylates







Cu2(OH)3(X).zH2O



Long range magnetic Order: Dipolar Interactions

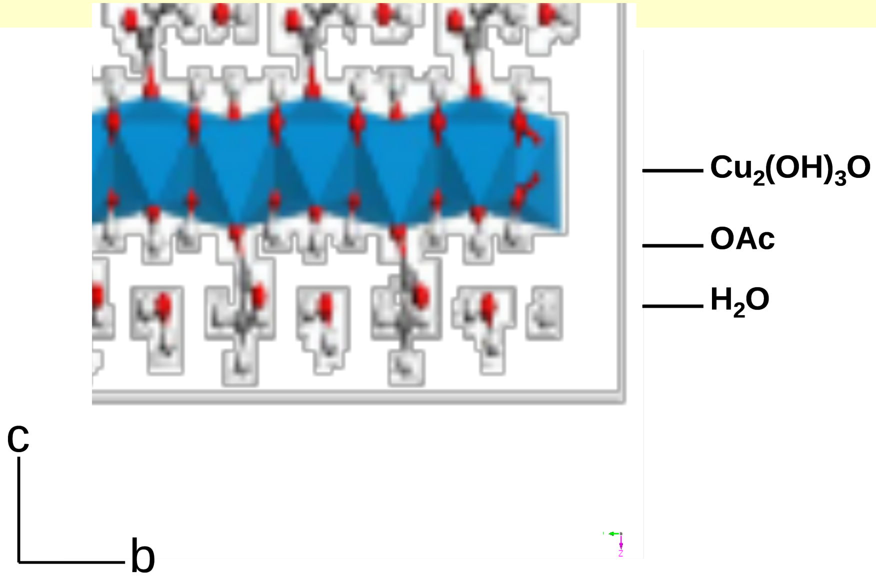
Critical distance ~ 10 Å

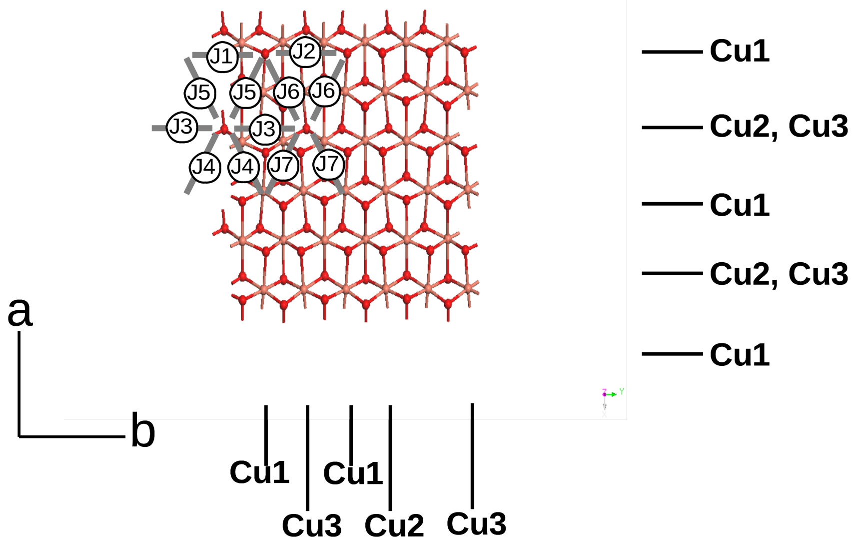
« Chemical pressure »

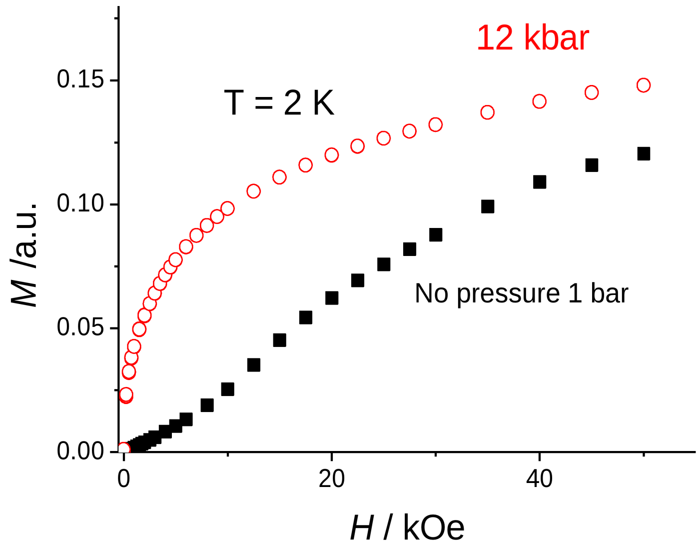
>> cooperative structural modification of the [Cu2(OH)3]+ layers

Rabu, Drillon, Awaga, Fujita, Sekine – in « Magnetism : Molecules to Materials II », Wiley-VCH, 2001

Cu2(OH)3(CH3COO)H2O a “frustrated” system







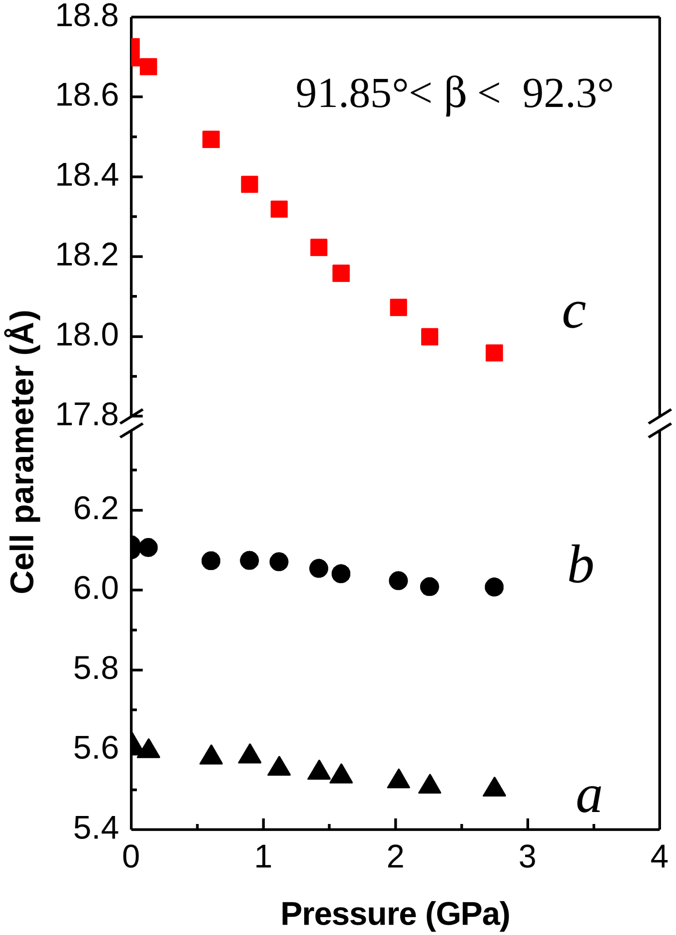
Pressure-induced Ferromagnetism

K. Suzuki, J. Haines, P. Rabu, K. Inoue, M. Drillon, J. Phys Chem C (2008), 112(48), 19147-1915

Structure from S. Švarcová, et al., *Cryst. Res. Tech.* **2011**, *46*, 1051.

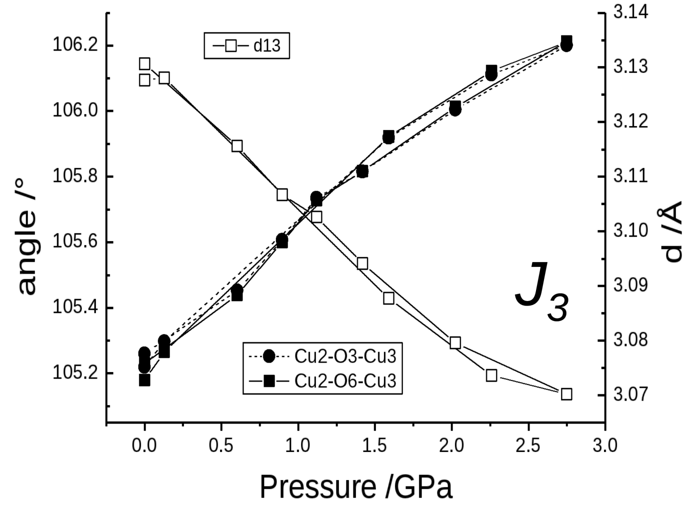
Powder X-Ray diffraction under pressure

2(OH)3(CH3CH2COO)H2O ;   dP=0 GPa = 9.3 Å



Monoclinic
P21/m

Reversible



More AF; more intense:
« **Frustration** » increases

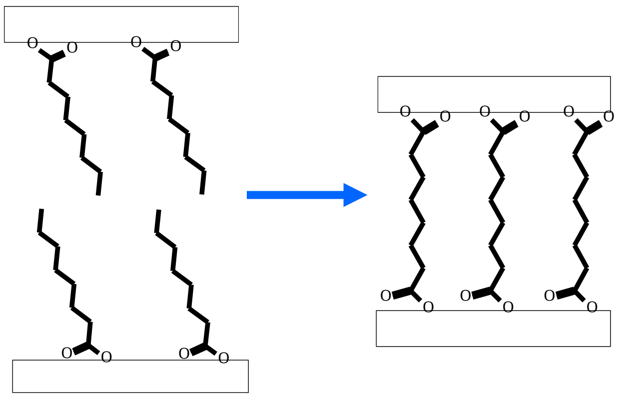
Subtle competition between **7 interactions**
>> magnetic state

Distribution ofJahn-Teller axes?

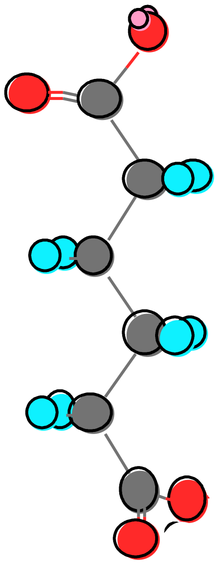
Supported by DFT calculations

J. Phys. Chem. C (**2008**) 112(48), 19147-19150

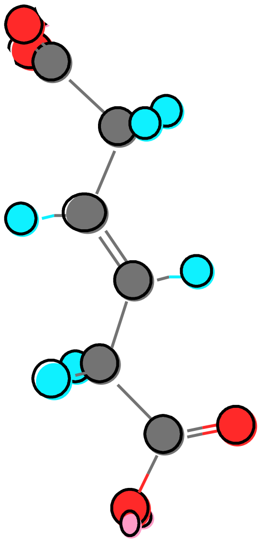
Role of conjugation along interlayer bridges



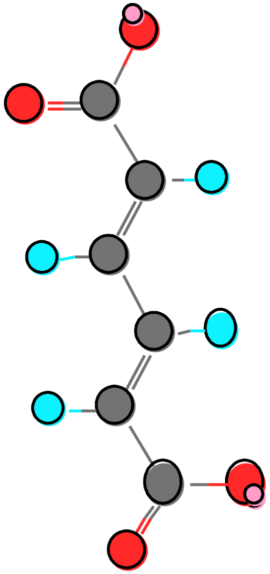
Inter-lamellar distance
d001 ≈ 10.3 Å



8.24 Å



8.14 Å

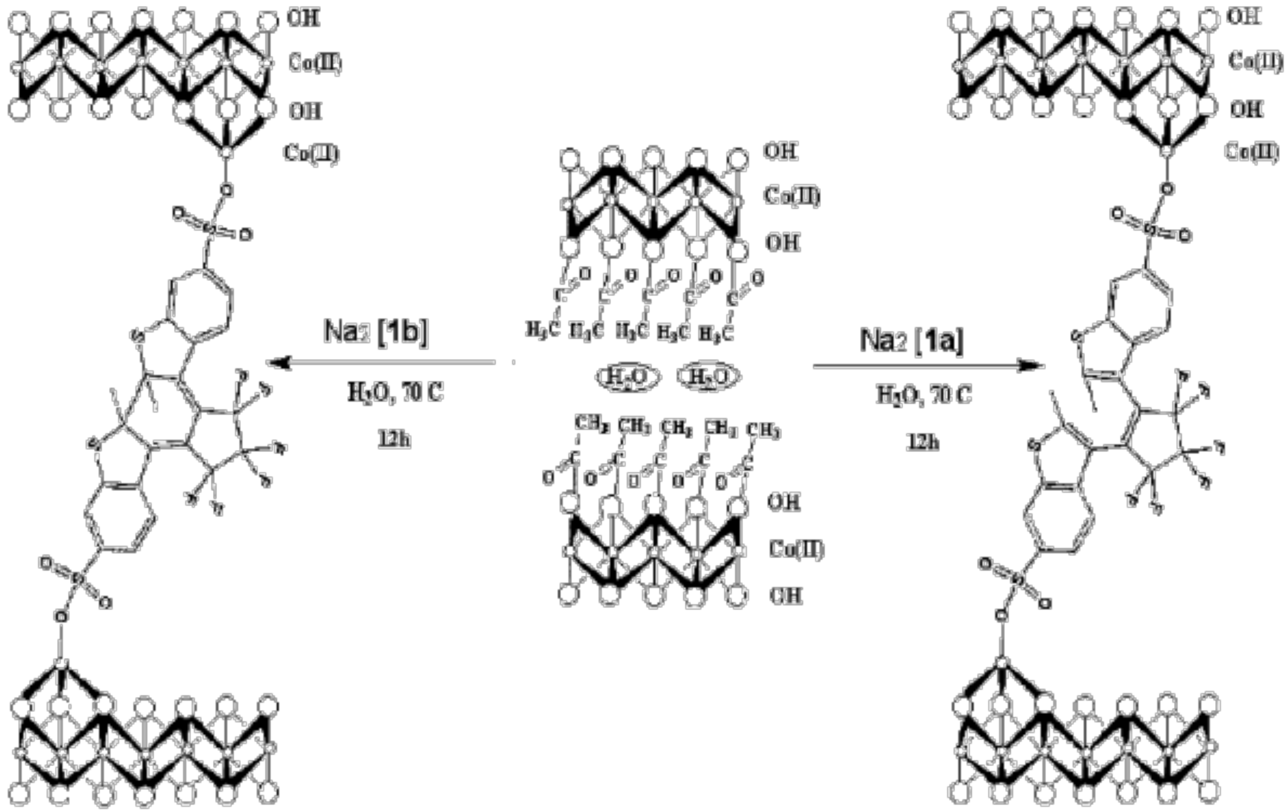


8.45 Å

2D	F	F	F
3D	AF	F	AF

NMR : spin polarisation

DAE in Cobalt(II) hydroxydes

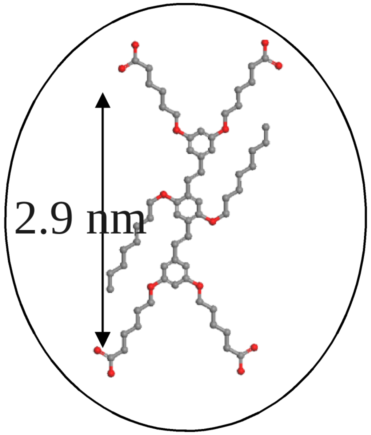


T_N = 20 K

T_N = 9 K

H. Shimizu, M. Okubo, A. Nakamoto, M. Enomoto and N. Kojima, *Inorg. Chem.*, 2006, **45**, 10240-10247.

Multifunctional Magnets

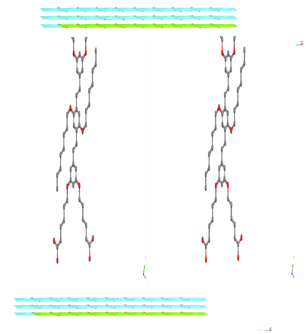


H4OPV

(idem Co(II), Ni(II), Cu(II))

Ni(NO3)2.6H2O
2.5 eq. KOH

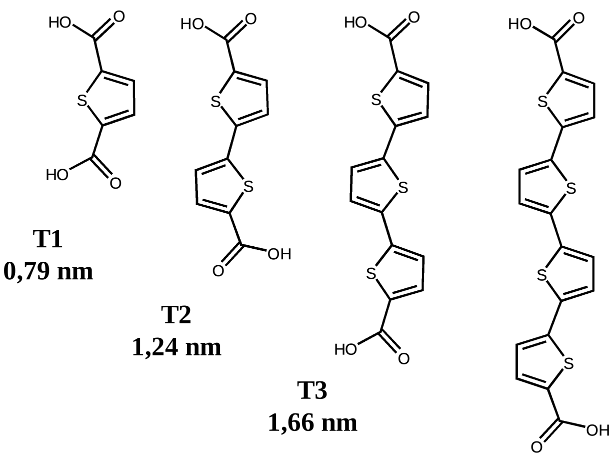
pH = 9-10
T = 25 °C; 72 h



Ni[OPV(COO)4]0.45(OH)0.2•2,6H2O

Luminescent magnets +synergy

Chem. Mater., **2004**, *16*, 2933.
J. Mater. Chem., **2009**, 19, 6106–6115



T1
0,79 nm

T2
1,24 nm

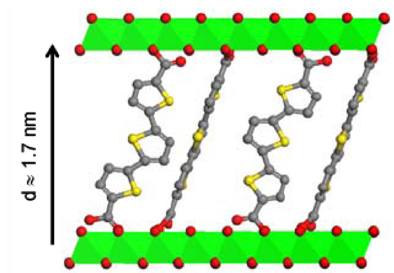
T3
1,66 nm

T4
2,09 nm

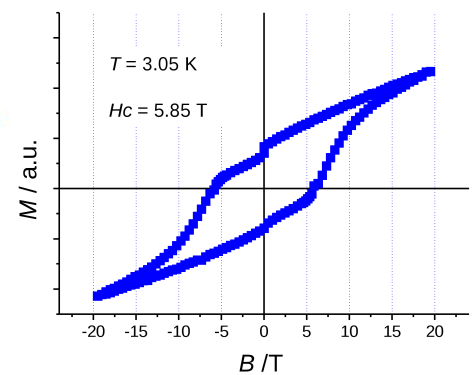
hydrothermal synthesis:
CoCl2.6H2O
NaOH

120-180 °C
20-60 hrs

(idem Co(II), Ni(II), Cu(II))



Hard magnets

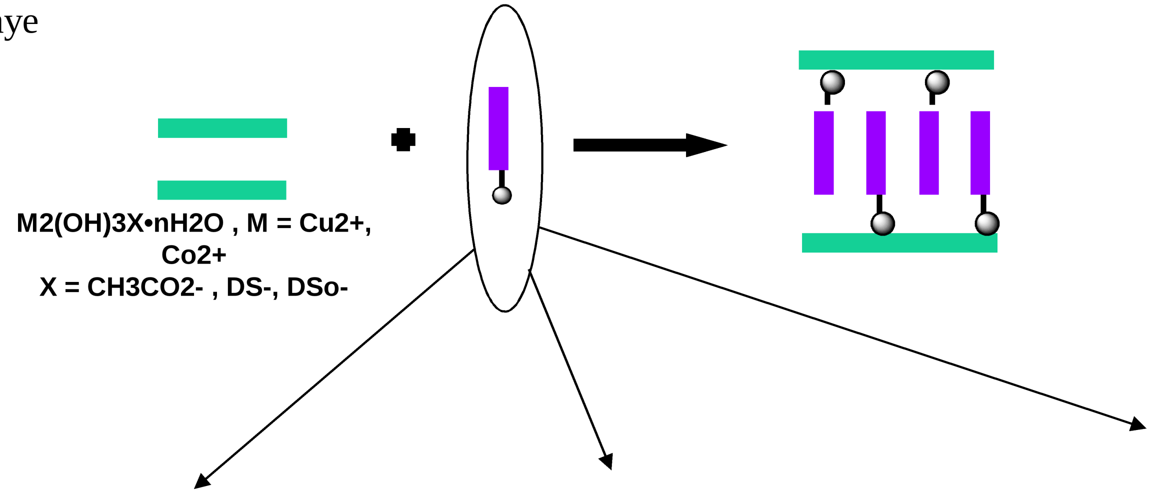


Co-T1, Hc = 6T at 3K
coll. S. de Brion

J. Mater Chem.., **2010**, 20, 9401-9414
Chem. Mater. 2006, Inorg. Chem. 2007

Functionalization with transition metal complexes

ANR COORDHYB
Post-doc Delahaye
PhD Eyele



Phthalocyanines MPcTsNa4
M = CuII, NiII, CoII

Dye,
Paramagnetic probe

Complexes « salen »
M = CuII, NiII, CoII, MnIII, FeIII, …
X = SO3Na, COONa
Chiral magnets

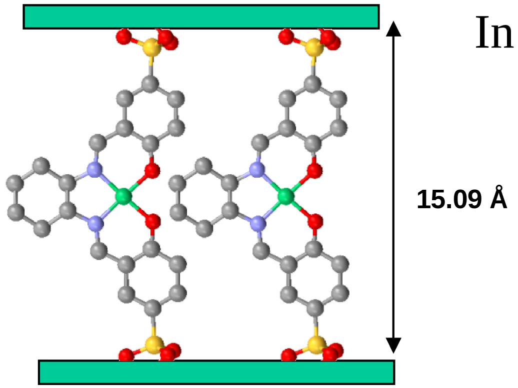
Complexes Ru(II) polypyridine

Luminescent magnets

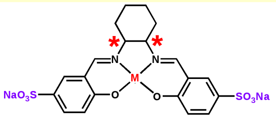
Photoexcitation: Triplet states, long living excited states

Dalton Trans., **2010**, *44*, 10577-10580.
Eur. J. Inorg. Chem., **2010**, *28*, 4450-4461
Eur. J. Inorg. Chem., **2012**, *32*, 2731-2740
Eur. J. Inorg. Chem., **2012**, *32*, 5225–5238

Insertion of the chiral Ni Cysalen complex into Co hydroxide

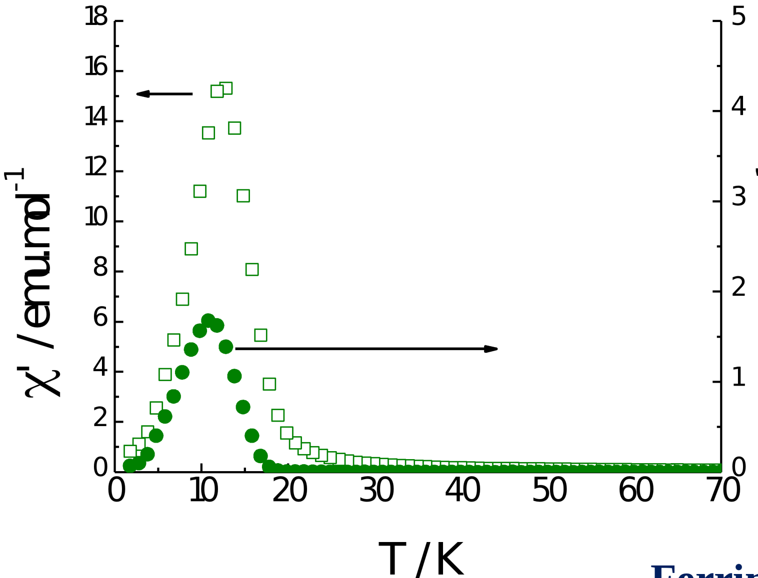


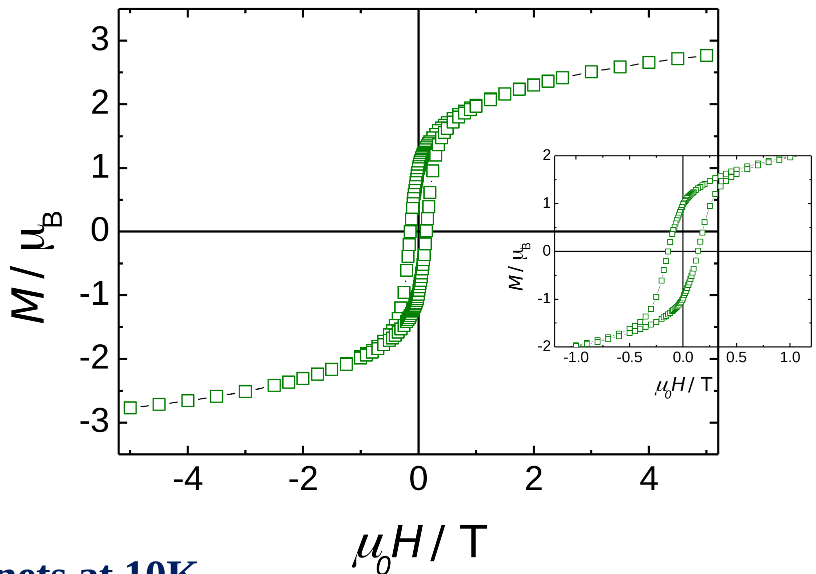
In Co hydroxide



Ni((R,R)CySalenSO3)⊂Co

Ni((S,S)CySalenSO3)⊂Co





Ferrimagnets at 10K

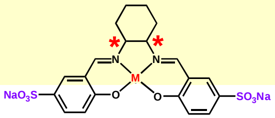
Ac susceptibility

M = f(*H*)

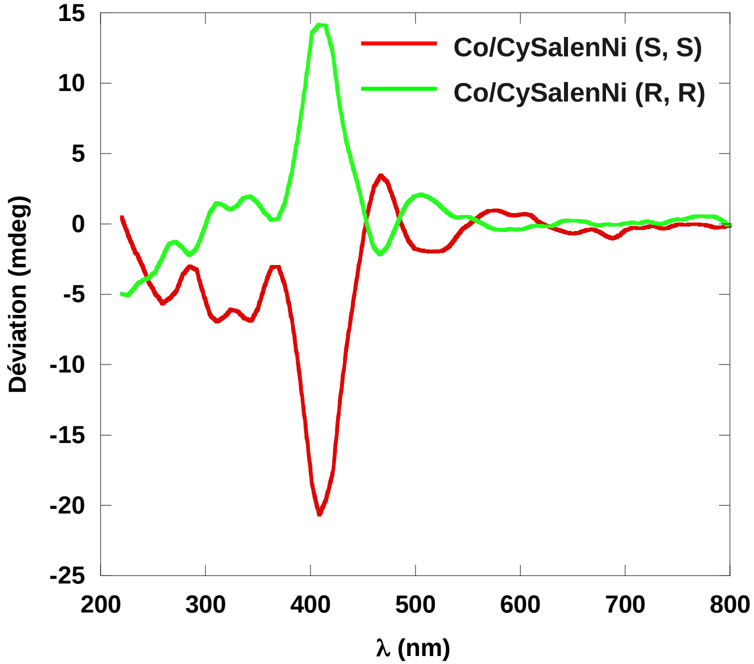
(μ0*Hac* = 0.35 mT, f = 100 Hz)

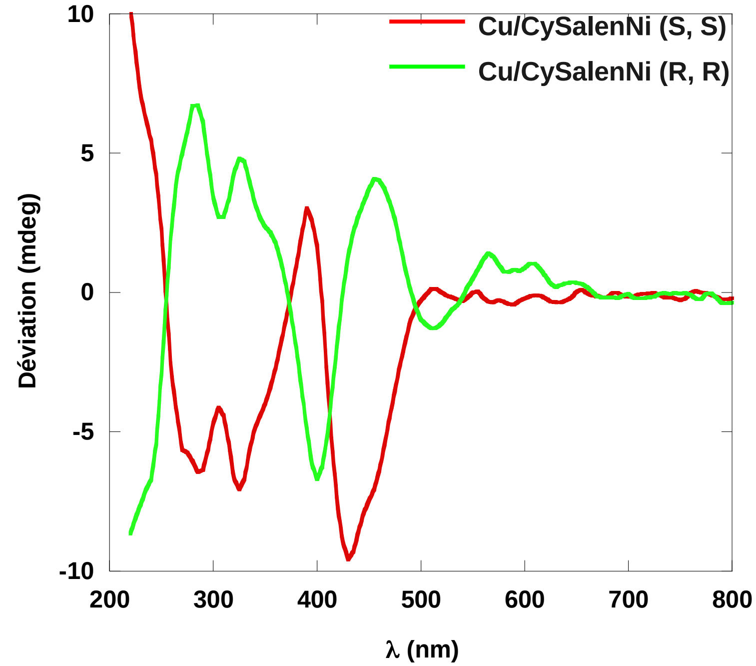
(T = 1.8 K)

Insertion of the chiral Ni Cysalen complex



Optical Circular Dichroism :





Chirality is maintained in the hybrid compounds !

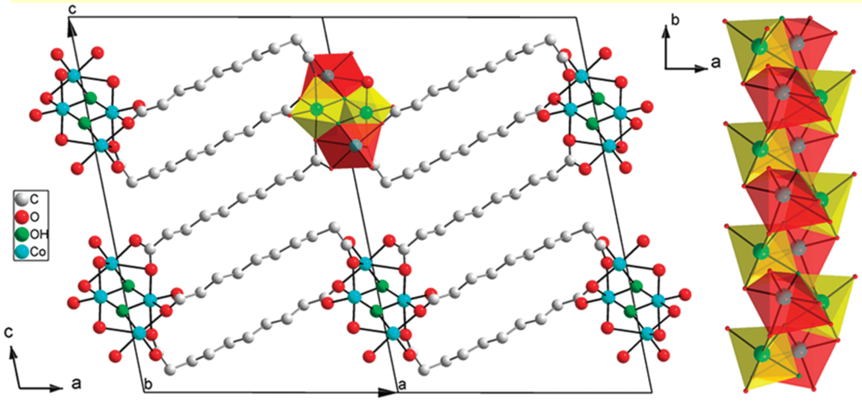
Influence of the metal inside the layers

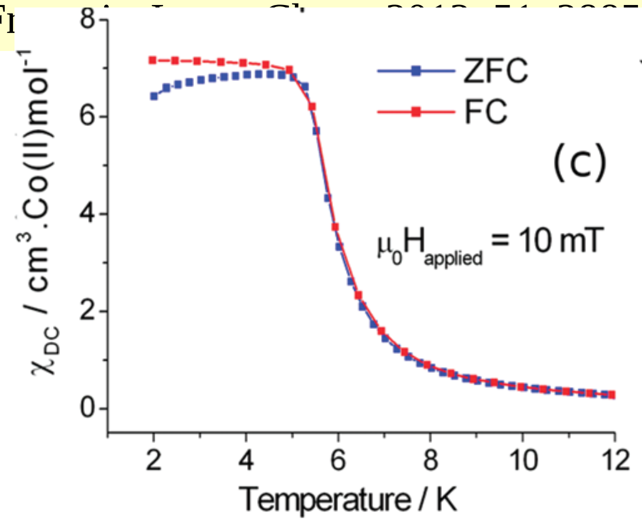
Promising for magneto chiral effects

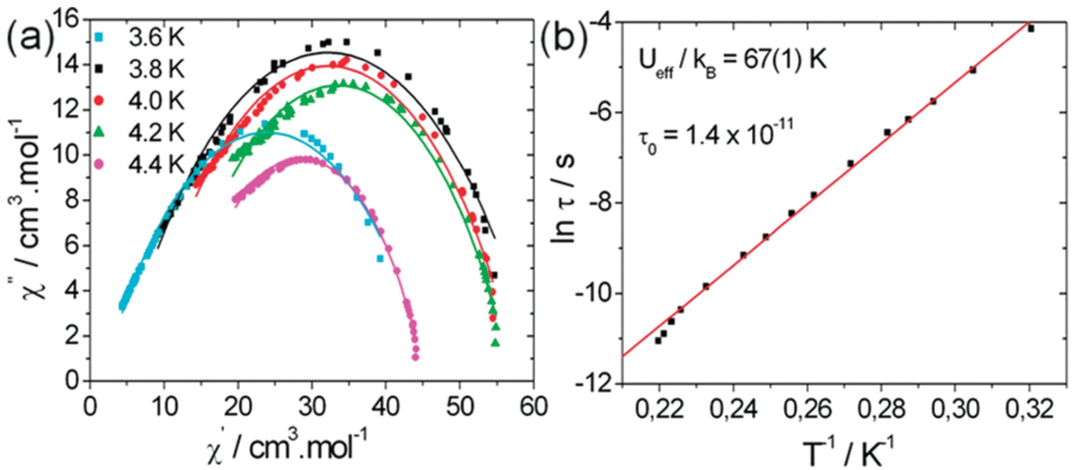
Emilie Delahaye
Dalton Trans., 2010, **39**, 10577–10580

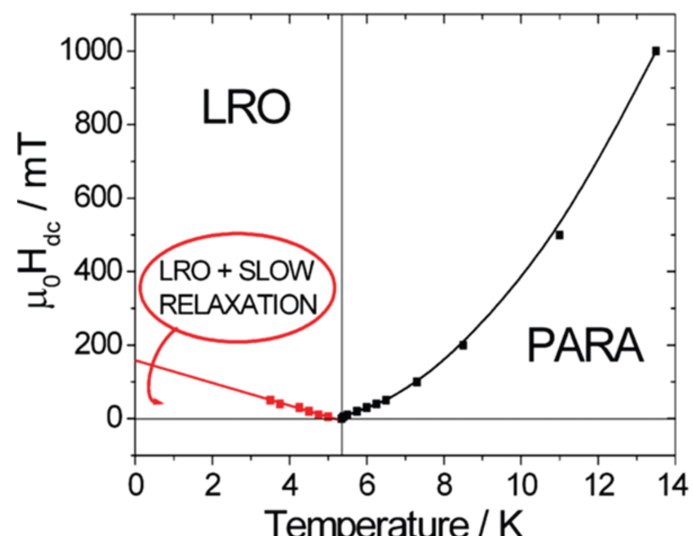
Co4(OH)2(C10H16O4)3 Metal−Organic Framework: Slow Magnetic Relaxation in the Ordered Phase of Magnetic Chains

R. Sibille,* T. Mazet, B. Malaman, T. Gaudisson, and M. Fr −2892



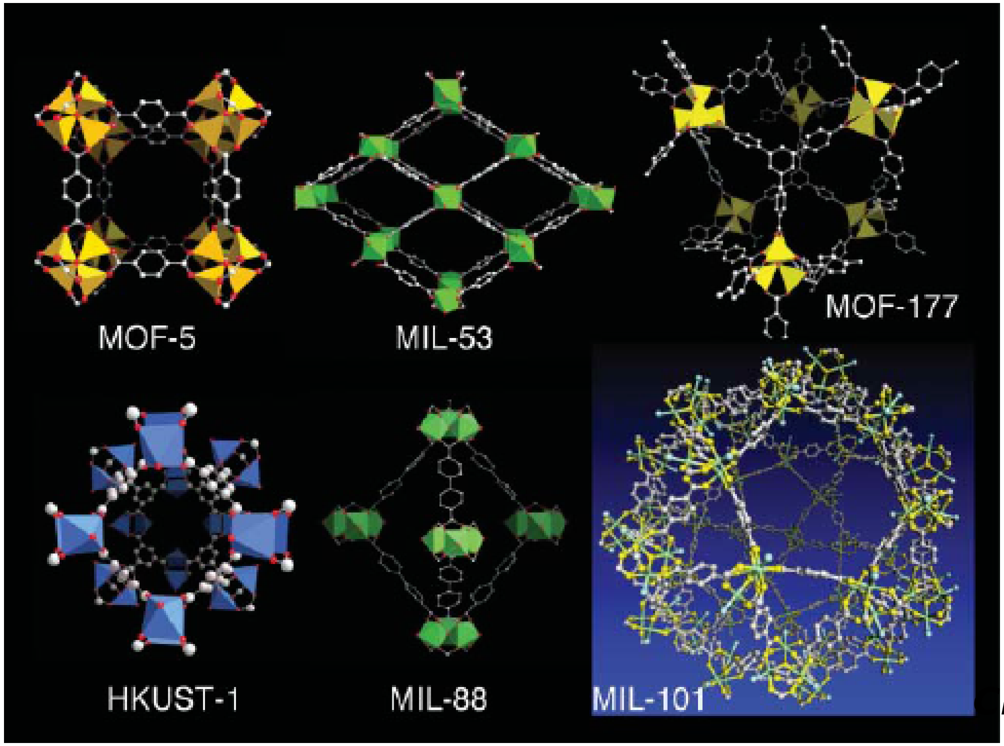




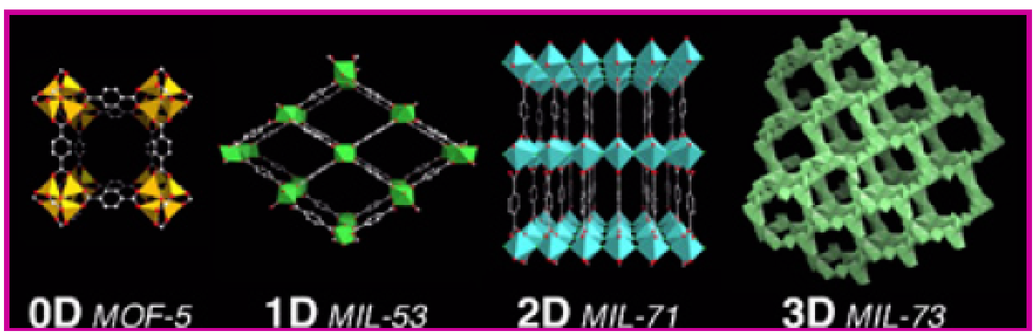


Anisotropie, transition 1D – 3D

Metal Oragnic Frameworks (MOFs)



G. Férey,
hem. Soc. Rev., 2008, **37**, 191 - 214

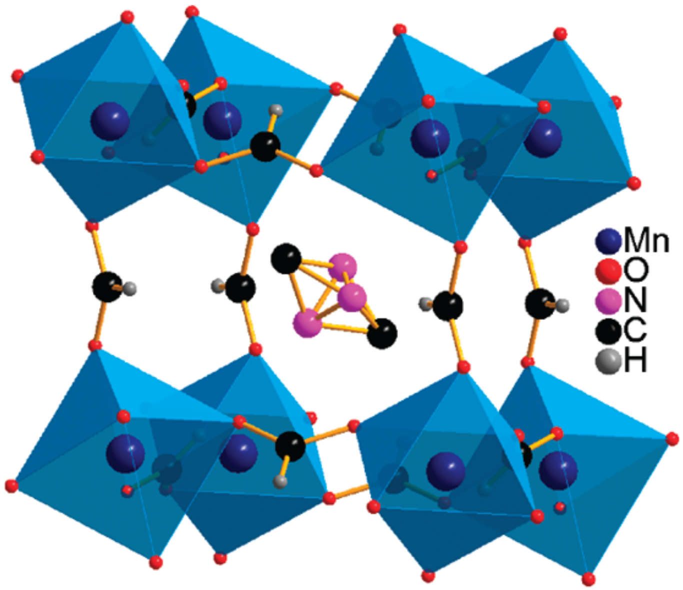


l'actualité chimique - janvier 2007 - n° 304

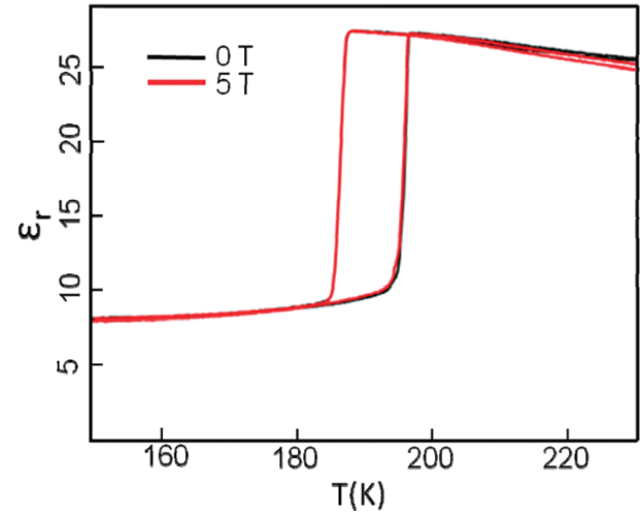
Chiral magnet: C. Livage et al. Chem. Commun., 2009, 4551–4553

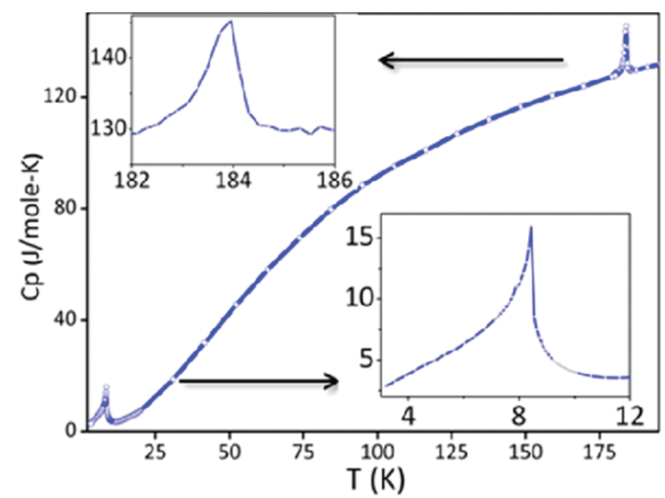
Porous magnets: J. Veciana et al. Chem Soc. Rev. 2007, 36, 770

Multiferroic Metal–Organic Framework



Building block of [(CH3)2NH2]Mn(HCOO)3, DMMnF.
The DMA cation (A) is at the center of a ReO3 type cavity, formed by manganese (B) and formate (X) ions.





P. Jain, N. S. Dalai, B. H. Toby, H.W. Kroto, A. K. Cheetham,
J. Am. Chem. Soc. 2008, 130, 10450; 2009, 131, 1“

Multiferroics

Electric Control of Magnetization and Interplay between Orbital Ordering and Ferroelectricity in a Multiferroic Metal–Organic Framework

Alessandro Stroppa et al.

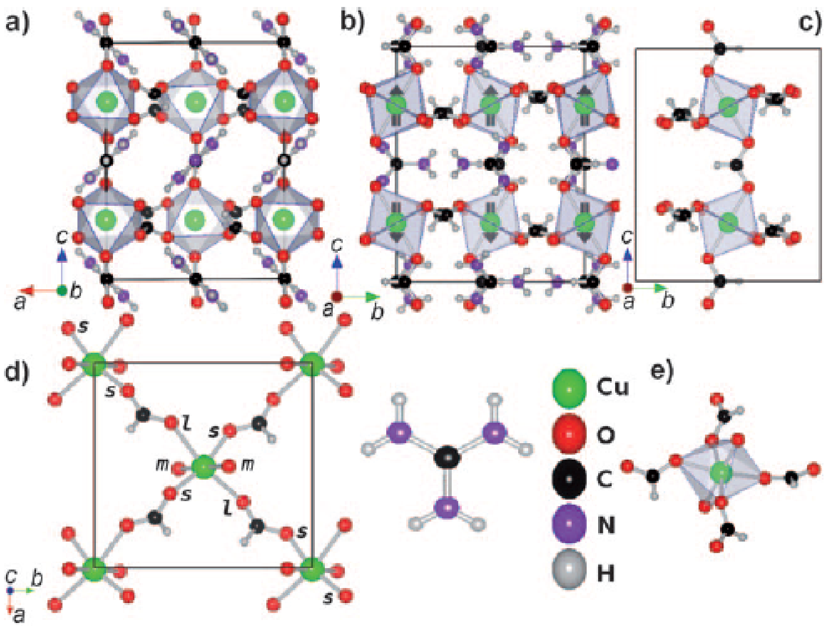


Figure 1. Crystal structure of $[C(NH_2)_3]Cu(HCOO)_3$. a, b) Side views. The octahedra are linked by HCOO groups, while the A sites of the perovskite network are occupied by $C(NH_2)_3$ groups. The spin config-

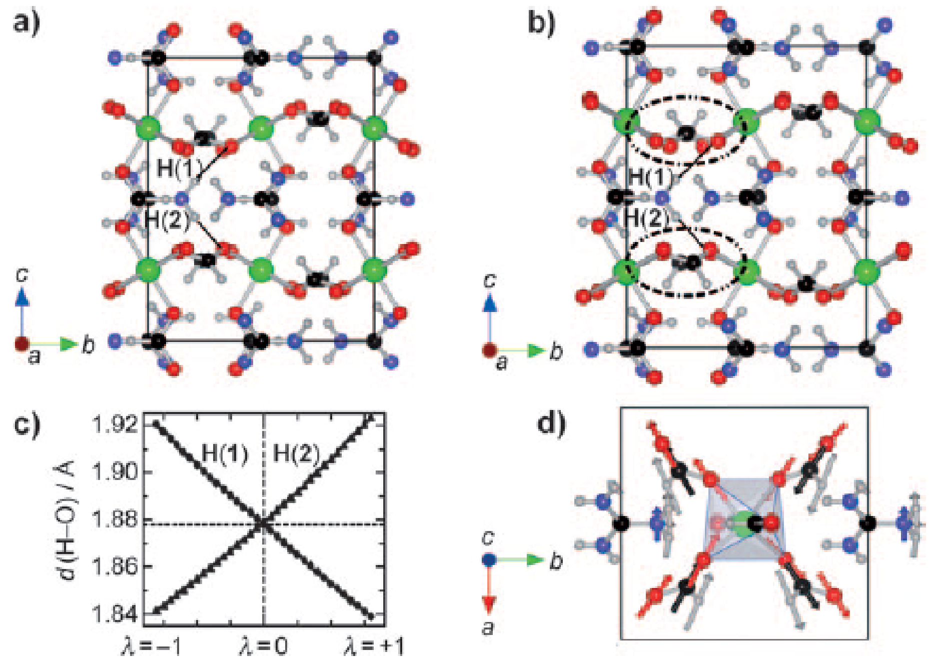


Figure 4. Coupling of the Jahn–Teller modes to A-group atoms through hydrogen bonding. a) Side view: hydrogen bonding in the centrosym-

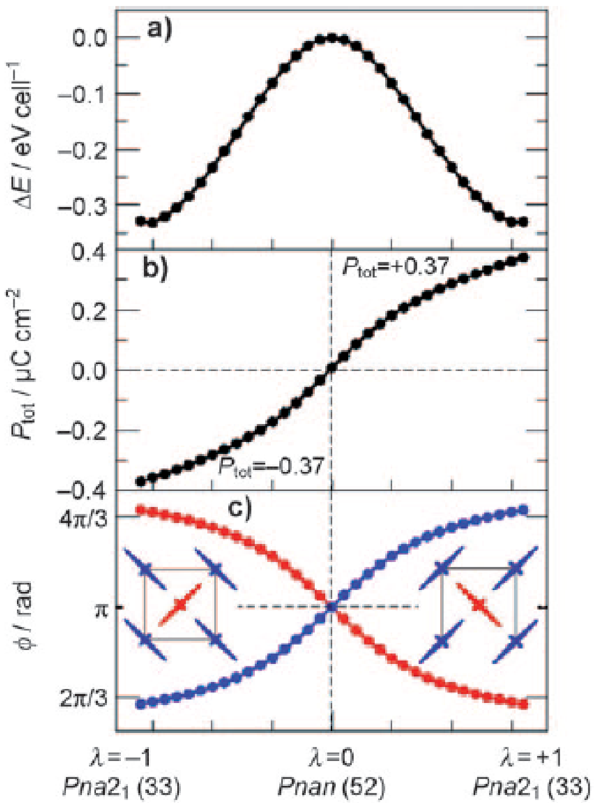


Figure 2. Path connecting the virtual nonpolar and the two polar phases with opposite polarizations. a) Total energy difference with respect to the paraelectric phase. b) The polarization P_{tot} as a function of λ. c) Evolution of the Jahn–Teller phases $\phi = \tan^{-1} Q_2/Q_3$ as a function of λ. Blue and red color refer to the two Cu sublattices with different direction of the elongation axis (*l*) in the *ab* plane.

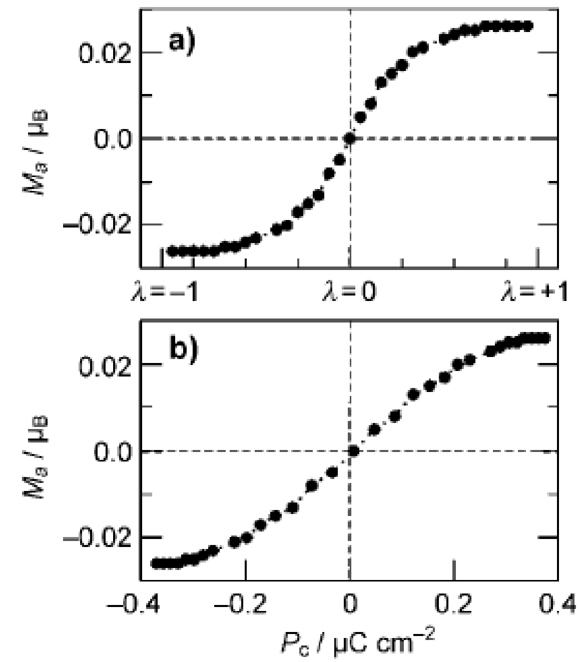
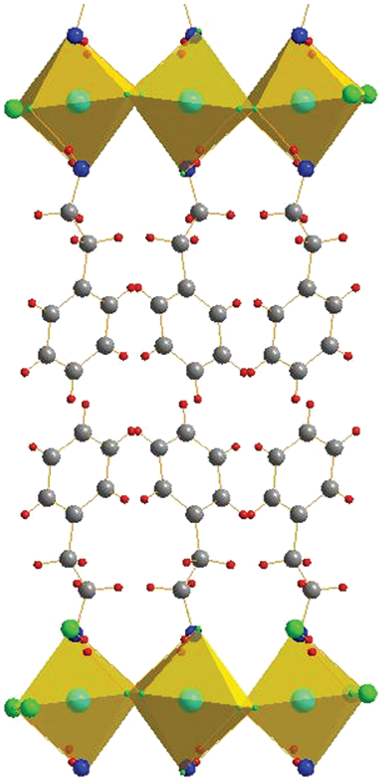
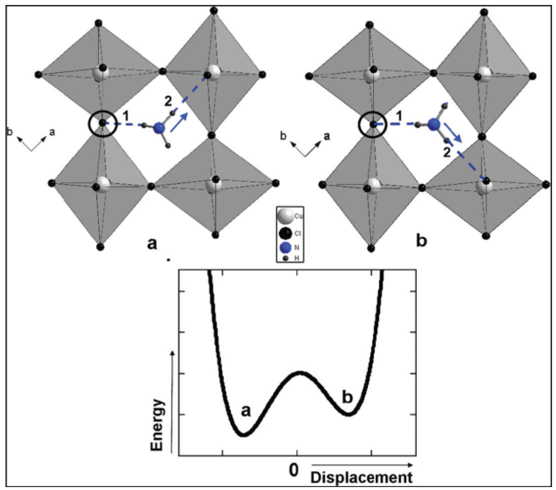


Figure 3. Electrical control of magnetization. a) Weak FM component as a function of the polar distortion and b) as a function of the polarization.

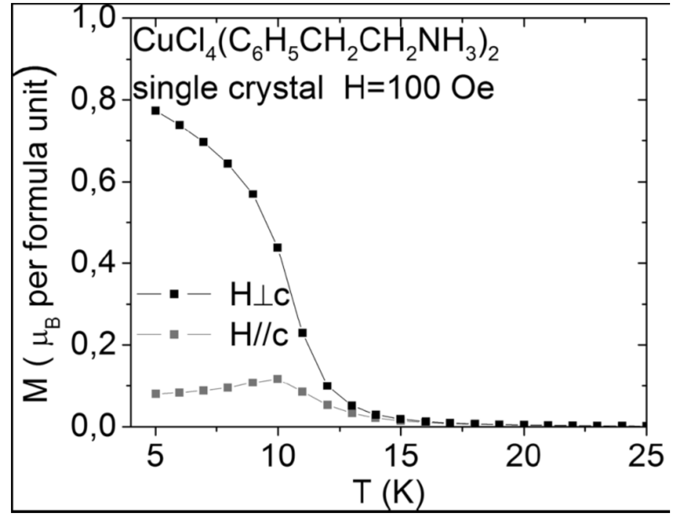
Hydrogen bond network and multiferroicity

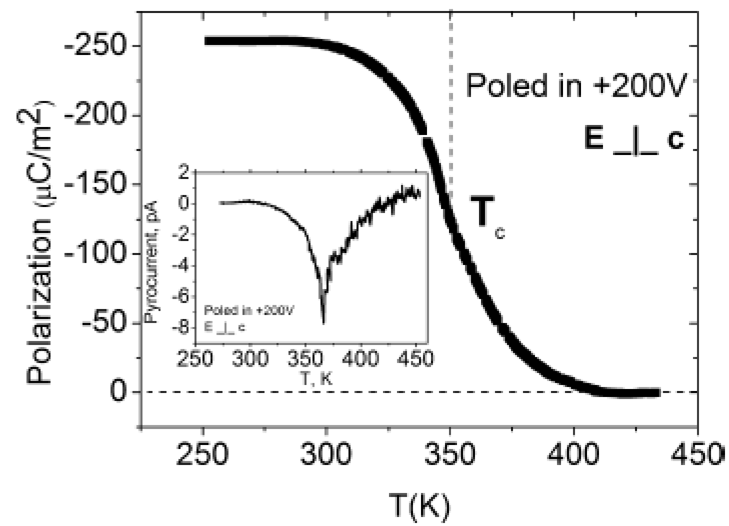
Thomas T. M. Palstra et al. Chem. Mater. 2012, 24, 133−139





$CuCl4(C6H5CH2CH2NH3)2$ at 100 K

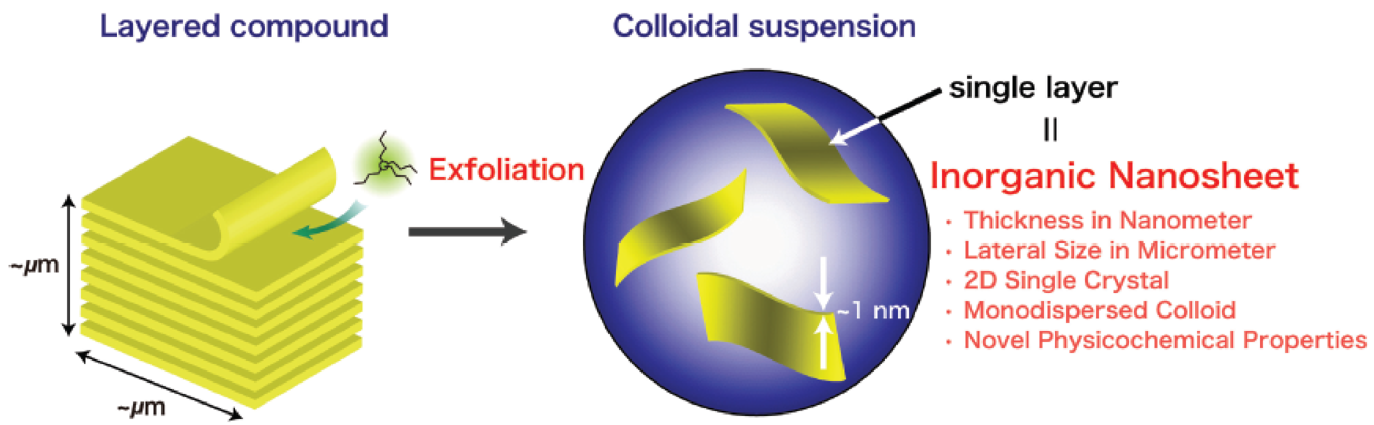




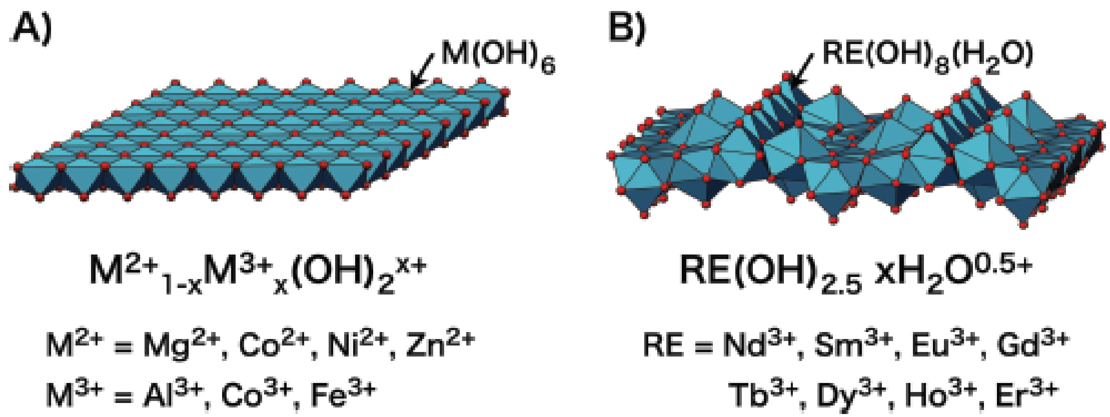
By *Renzhi Ma* and *Takayoshi Sasaki* *

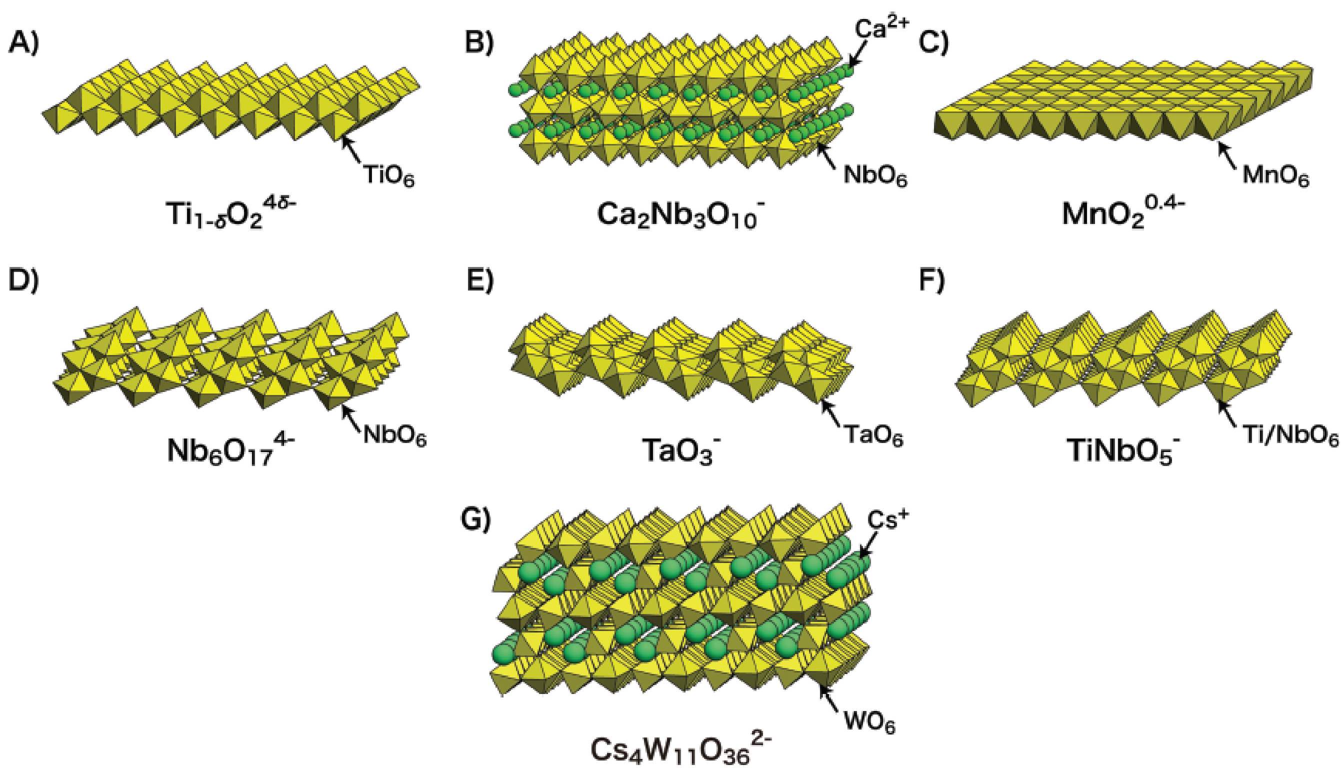
Nanosheets of Oxides and Hydroxides: Ultimate 2D Charge-Bearing Functional Crystallites

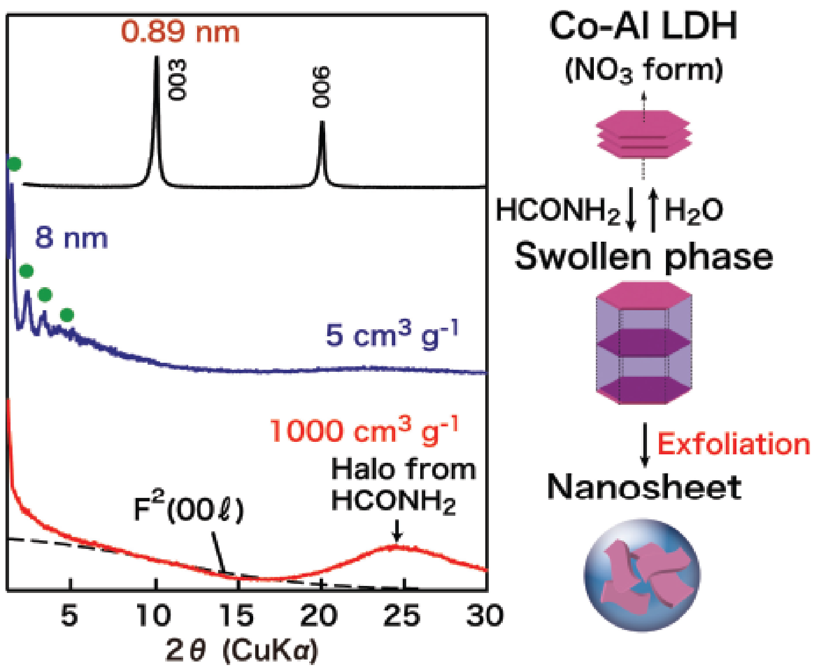
Adv. Mater. **2010**, *22*, 5082–5104



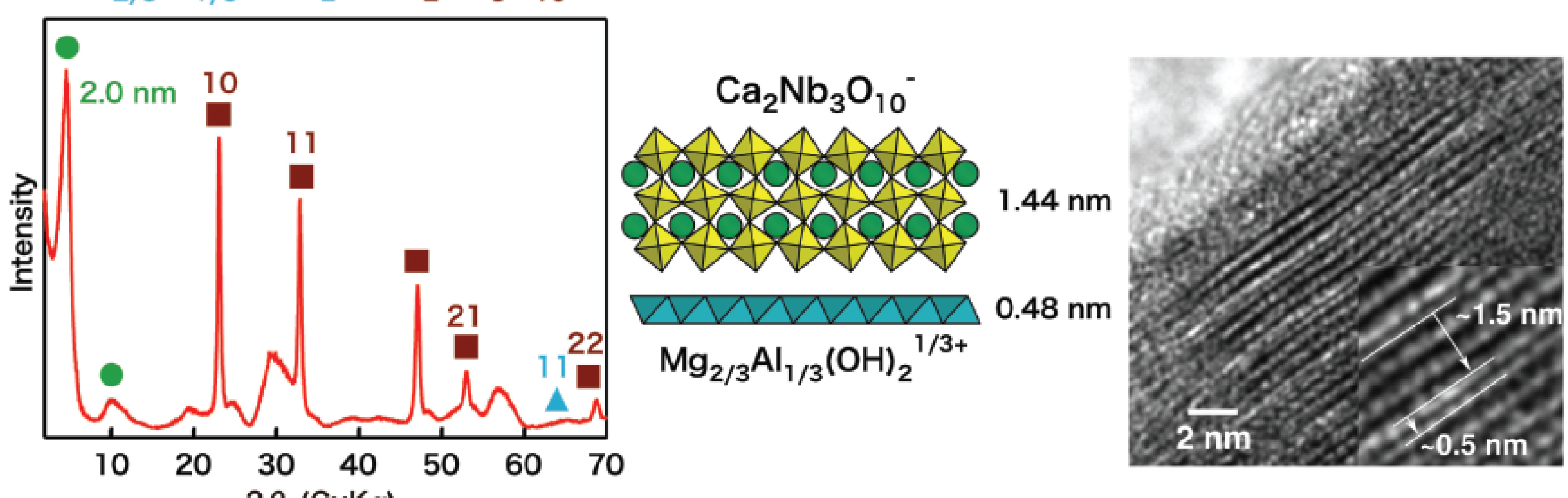
Schematic model illustrating the exfoliation of a layered compound into colloidal nanosheets.


A)
$M(OH)_6$
B)
$RE(OH)_8(H_2O)$
$M^{2+}_{1-x}M^{3+}_{x}(OH)_2^{x+}$
M^{2+} = Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}
M^{3+} = Al^{3+}, Co^{3+}, Fe^{3+}
$RE(OH)_{2.5}\ xH_2O^{0.5+}$
RE = Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}
Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}


A)
TiO_6
$Ti_{1-\delta}O_2^{4\delta-}$
B)
Ca^{2+}
NbO_6
$Ca_2Nb_3O_{10}^-$
C)
MnO_6
$MnO_2^{0.4-}$
D)
NbO_6
$Nb_6O_{17}^{4-}$
E)
TaO_6
TaO_3^-
F)
Ti/NbO_6
$TiNbO_5^-$
G)
Cs^+
WO_6
$Cs_4W_{11}O_{36}^{2-}$



B) $Mg_{2/3}Al_{1/3}(OH)_2$ / $Ca_2Nb_3O_{10}$



Co-existence of supraconductivity and magnetism

E. Coronado et al. Nature Chem. 2010, 1031

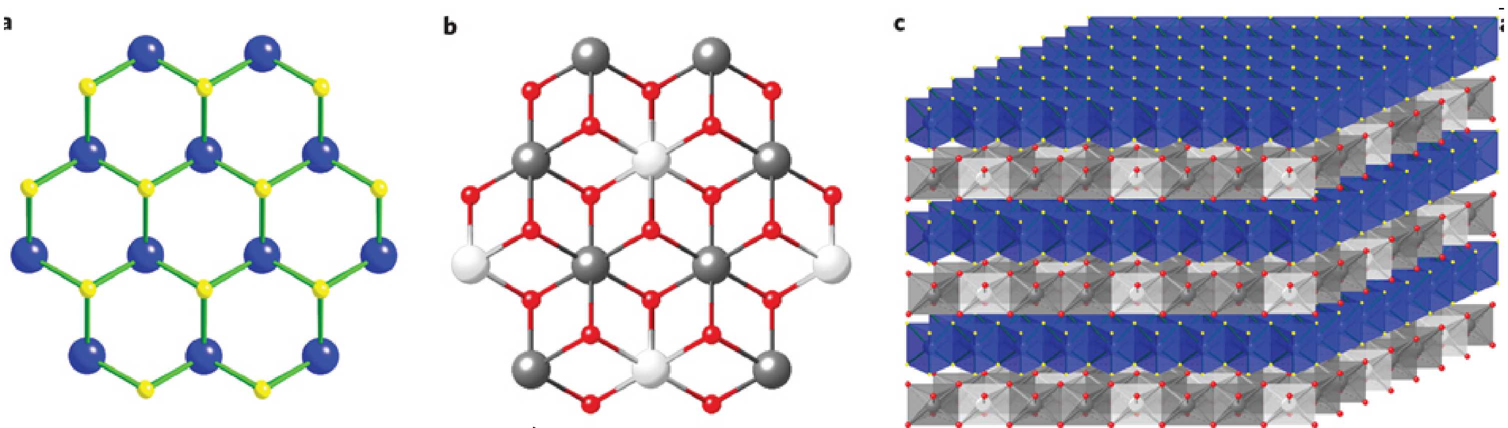
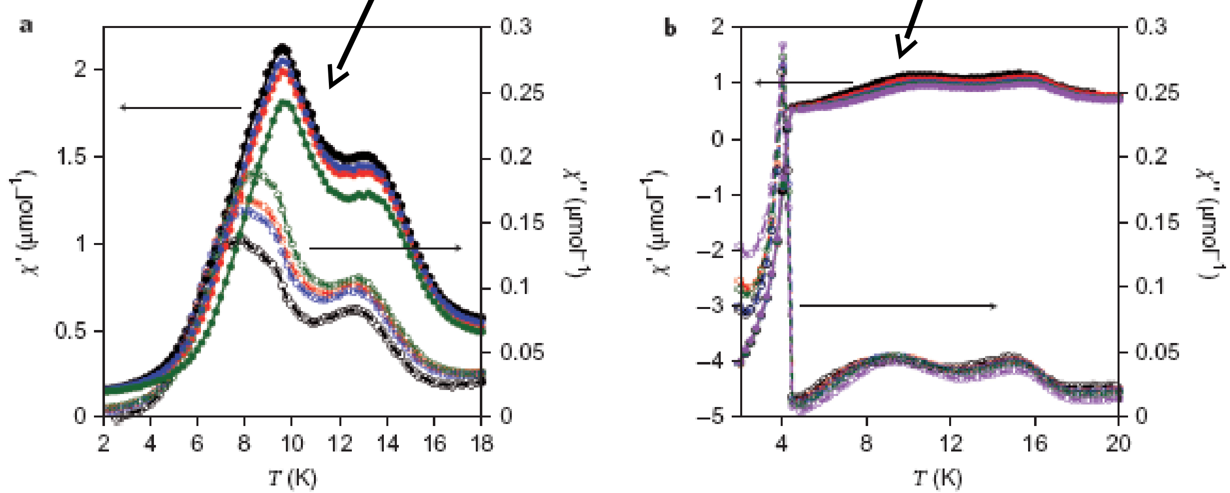
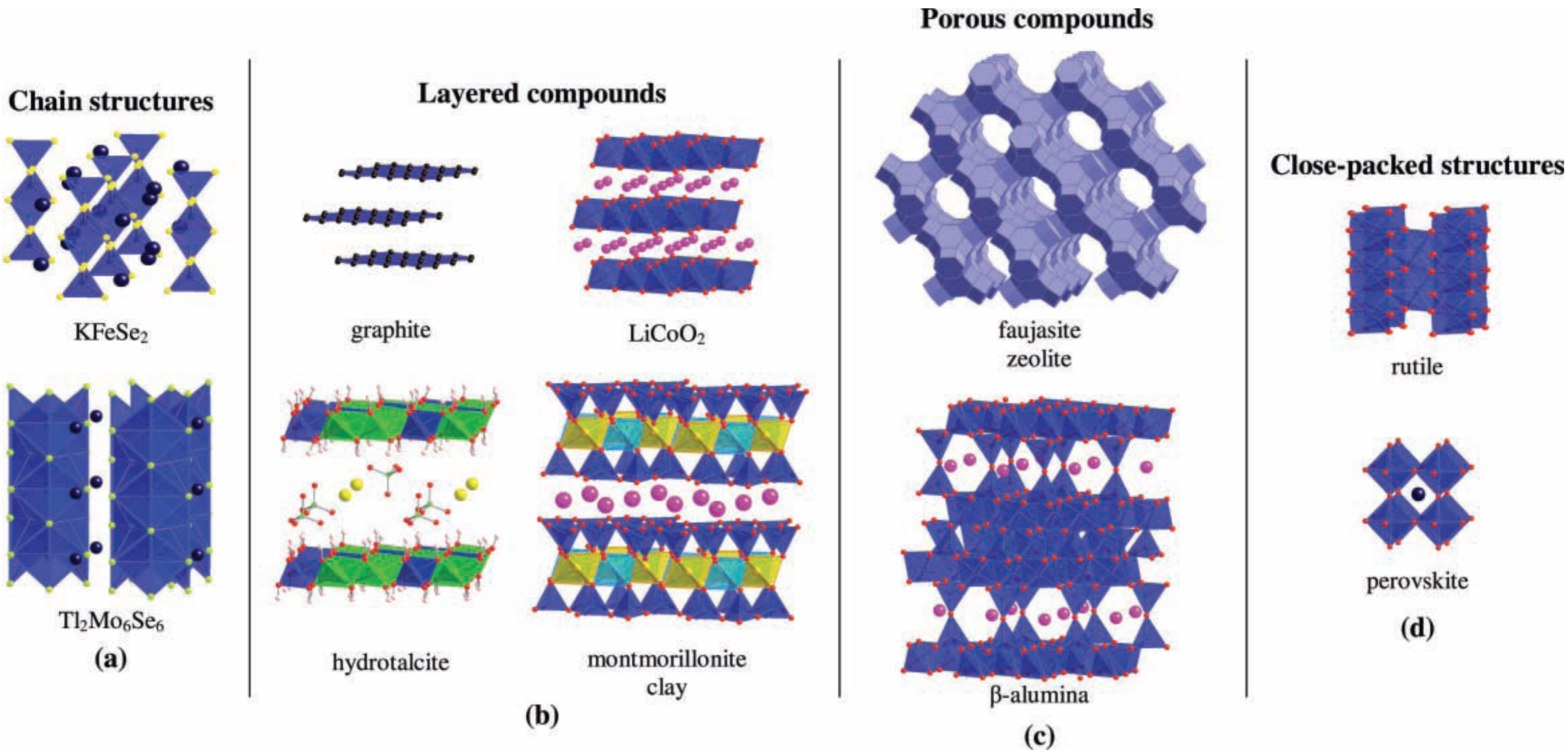


Figure 1 | Schematic representation of the layered components and the restacked material. a, View of the $[TaS_2]^{-0.33}$ superconducting layer (Ta, blue spheres; S, yellow spheres). **b**, View of the $[Ni_{0.66}Al_{0.33}(OH)_2]^{+0.33}$ magnetic layer (Ni, grey spheres; Al, white spheres; O, red spheres). **c**, Representation of the restacked material along the *c* axis showing the alternating superconducting/magnetic layers.



$[Ni_{0.66}Fe_{0.66}(OH)_2^{+0.33}]\ [TaS_2^{-0.33}]$

Topochemical Manipulation



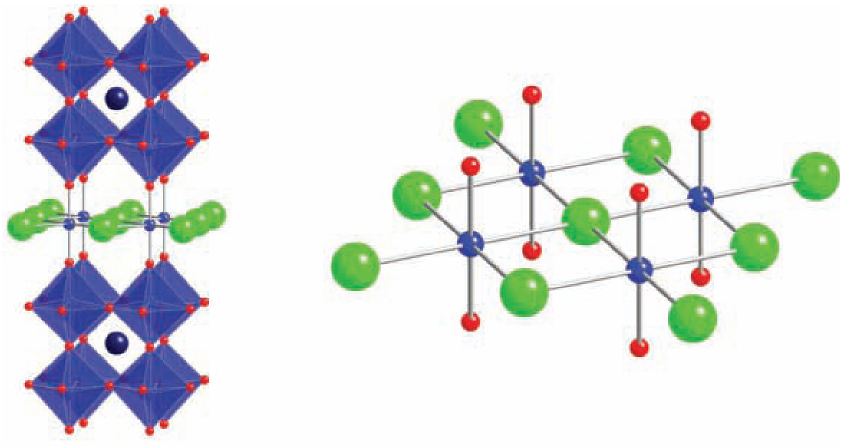
ion exchange, intercalation, layer extraction,
reductive deintercalation,
grafting, exfoliation, layer construction, pillaring,
substitution reactions

Adv. Mater. 2011, 23, 442–460

Topochemical Manipulation of Perovskites: Low-Temperature Reaction Strategies for Directing Structure and Properties

*K. G. S. Ranmohotti , E. Josepha , J. Choi , J.Zhang , and J. B. Wiley *, Adv. Mater. 2011, 23, 442–460*

$ALaNb_2O_7 + CuX_2 \rightarrow (CuX)LaNb_2O_7 + AX$ (X = Cl, Br)



$(MX)LaNb_2O_7$

(M = V, Cr, Mn, Fe, Co, Cu for X = Cl; M = Cu for X = Br); interlayer consists of unusual edge-sharing MO_2X_4 octahedra.

Frustrated AF with Spin-gap behavior

Kageyama et al. J. Phys. Soc. Japan 2005, 74, 1702

CONCLUSION

Approche moléculaire ou hybride ou composite

Bibliothèque de briques variées
Fonctionnalisation et Contrôle de la topologie
Systèmes ajustables ou adaptables
Multipropriétés

!!
Chimie complexe
Systèmes coopératifs mais peu denses (TC faibles)
Liaison entre briques (synergie)
Poudre/monocristal
La physique n'est pas toujours comprise