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Paramagnetic Ligands designed using Thiazyl Radicals

Photo collage credit: Danielle Dinsdale, M.Sc.

Kathryn E. Preuss

ESMolNa 2025, Santa Pola, Spain – May 20th, 2025

Acknowledgements

Student Contributors to this work

Michelle Mills (Ph.D. 2021)
Adam Maahs (Ph.D. 2017)
R. Alex Mayo (M.Sc. 2017)
Harrison Young (B.Sc. 2019)
Elisabeth Fatila (Ph.D. 2013)
Jian (Kyle) Wu (Ph.D. 2008)
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Julia Newman (M.Sc. candidate)
James Galvao (M.Sc. candidate)

Collaborators contributing to this work

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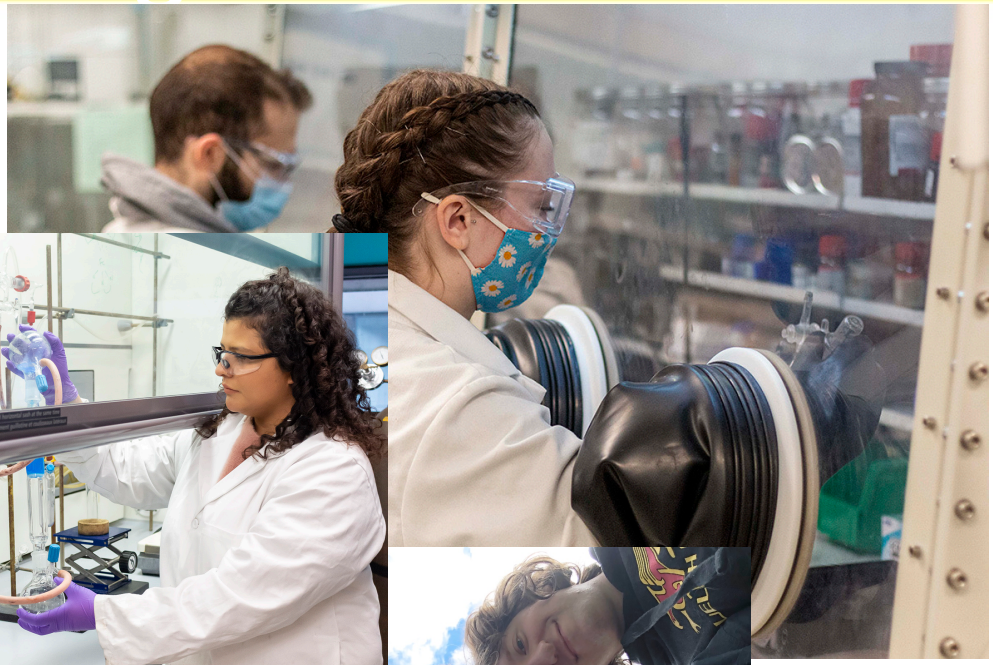
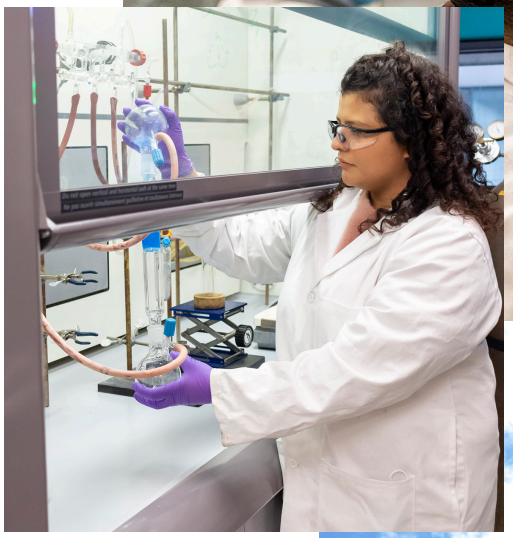
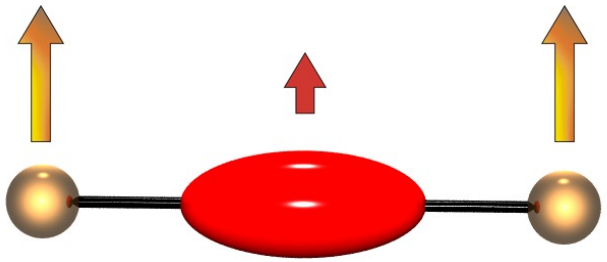
Prof. Tom Lancaster (Durham U.)
Dr. Alberto Hernández-Melián (Durham U.)
Prof. Dmitriy V. Soldatov (U. Guelph)
Prof. René T. Boeré (U. Lethbridge)



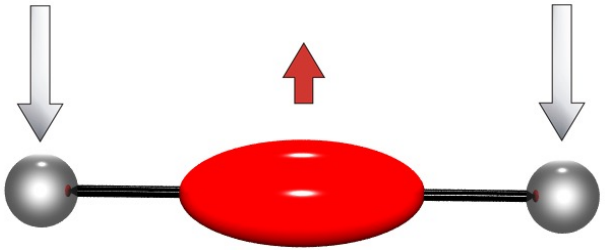


Paramagnetic Ligands – Why?

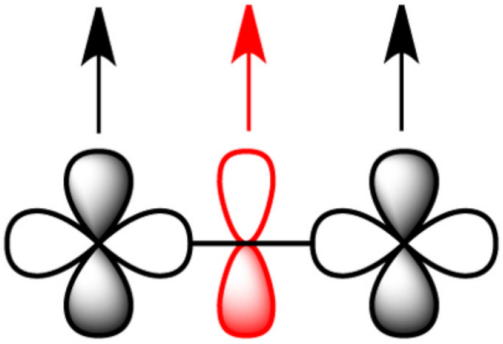
1) Mediate magnetic coupling between *hs* metal ions: $S_T > 0$



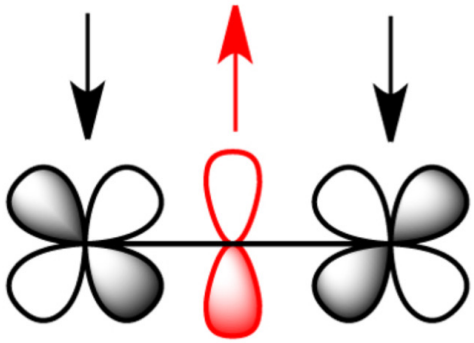
paramagnetic ligand
FM coupling



paramagnetic ligand
AF coupling



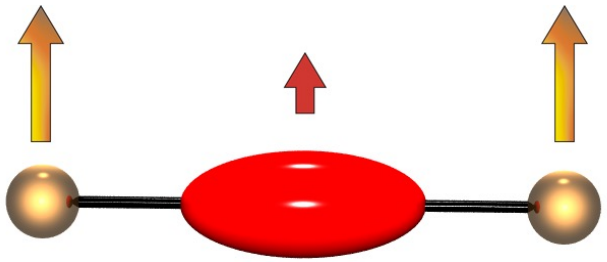
orthogonal



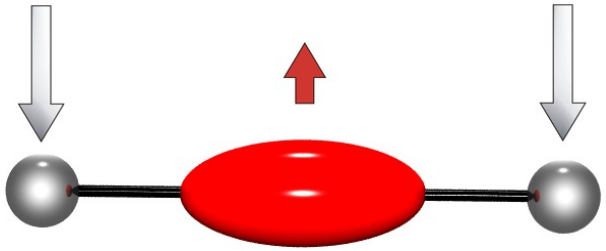
non-orthogonal

Paramagnetic Ligands – Why?

1) Mediate magnetic coupling between *hs* metal ions: $S_T > 0$



paramagnetic ligand
FM coupling



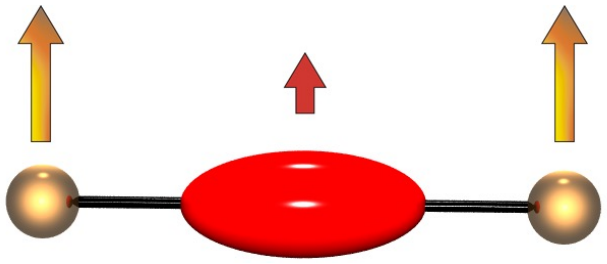
paramagnetic ligand
AF coupling

Design Options?

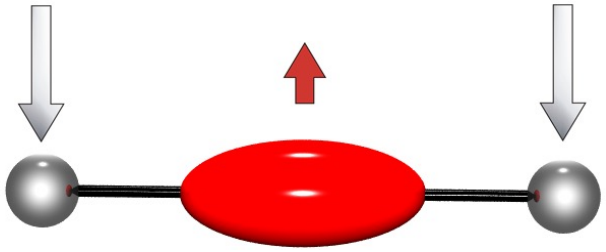
- Easy synthesis
- Large "window" of redox stability
- Good σ-donor

Paramagnetic Ligands – Why?

1) Mediate magnetic coupling between *hs* metal ions: $S_T > 0$

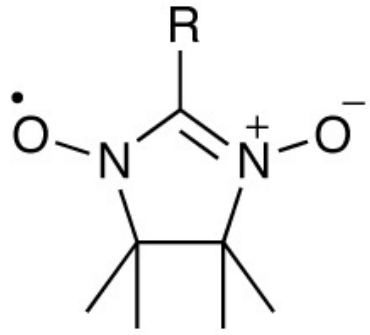


paramagnetic ligand
FM coupling

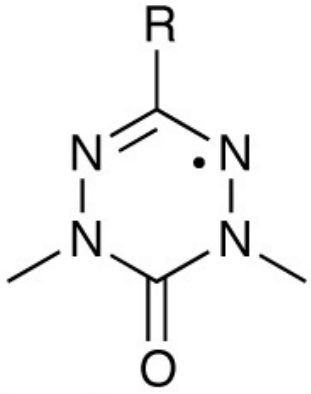


paramagnetic ligand
AF coupling

Design Options?



nitronyl nitroxides



(oxo)verdazyls

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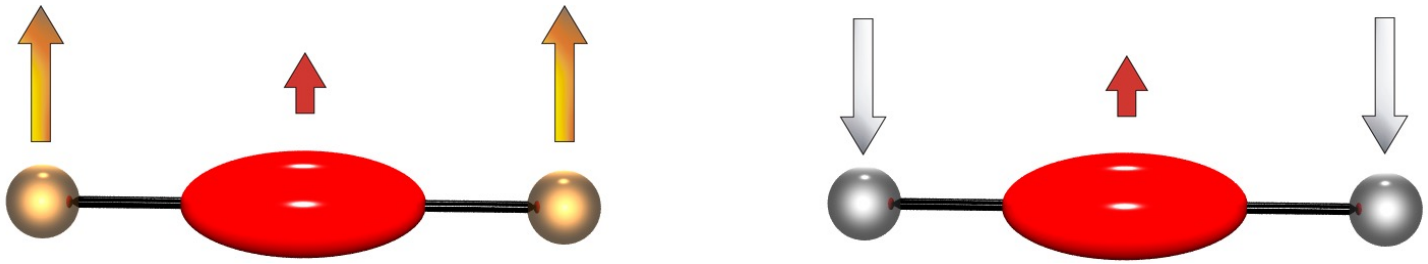
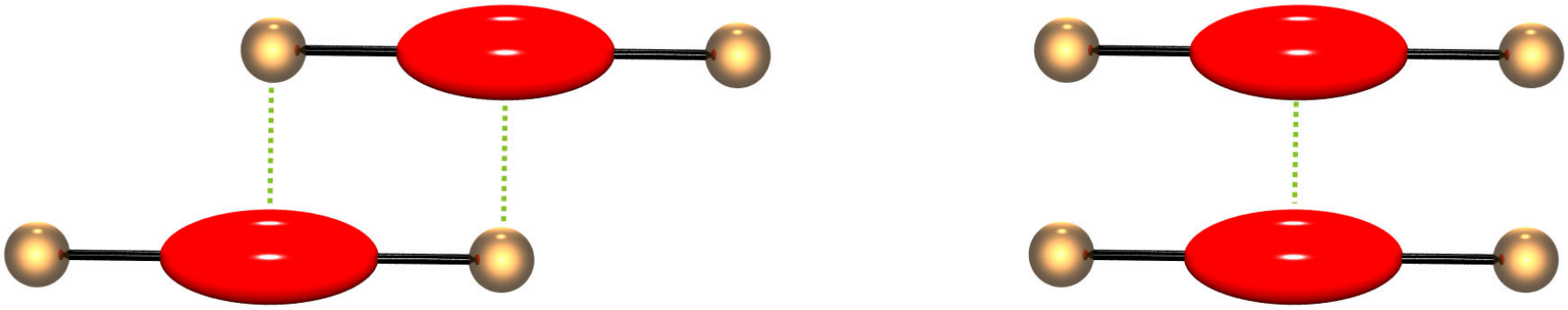
Paramagnetic Ligands – Why?

1) Mediate magnetic coupling between *hs* metal ions: $S_T > 0$



2) Mediate *intermolecular* interactions – magnetic, conductive, "switchable"



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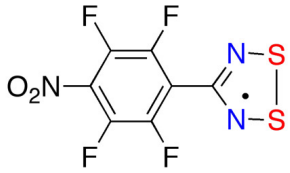
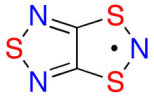
Thiazyl Radicals - Properties



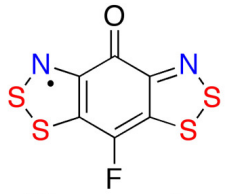
FM ordering < 1.6 K

J. M. Rawson, *et al.*,
Angew. Chem. Int. Ed., **2003**, *42*, 4782.



RT magnetic bistability

W. Fujita & K. Awaga,
Science, **1999**, *286*, 261.



Metallic conductivity > 3 GPa

R. T. Oakley, *et al.*,
J. Am. Chem. Soc., **2012**, *134*, 9886.

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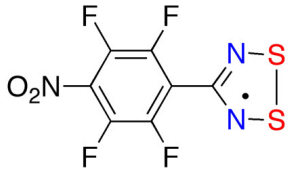
Thiazyl Radicals - Properties



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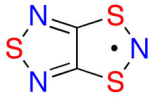

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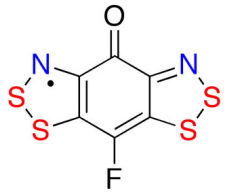

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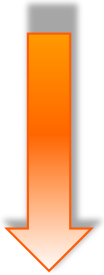

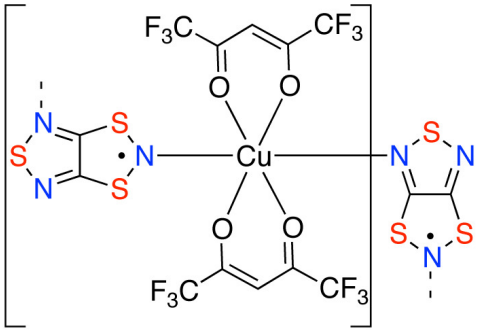

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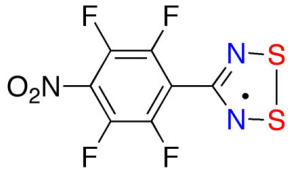

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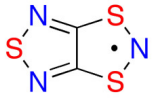

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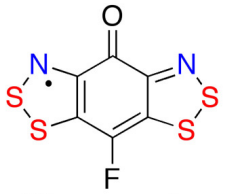

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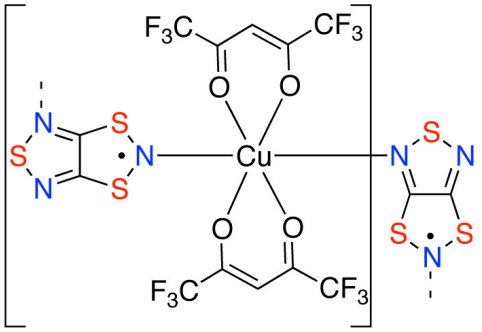

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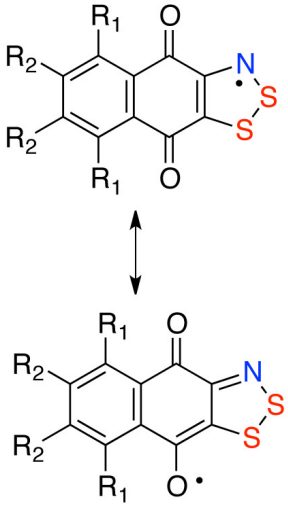
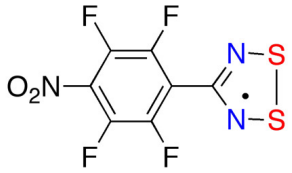


Preuss, *et al.*, *Chem. Commun.* **2012**, *46*, 10963.
Preuss, *et al.*, *Inorg. Chem.* **2021**, *60*, 11338.

Thiazyl Radicals - Properties



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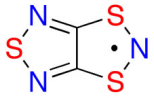

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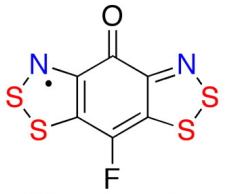

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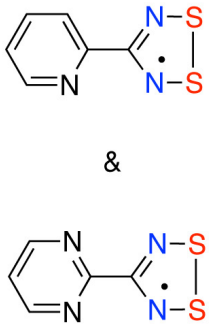
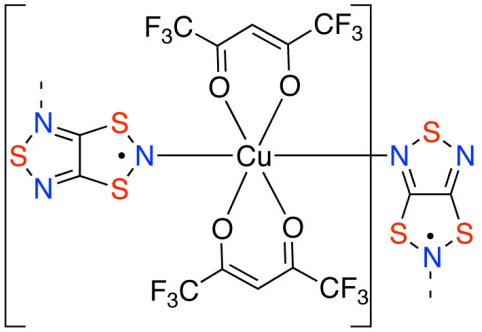


Preuss, *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 9942.
Preuss, *et al.*, *Chem. Commun.* **2006**, 341.



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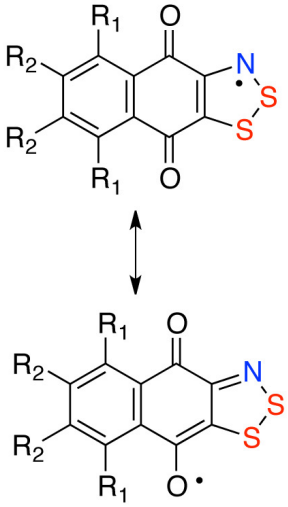
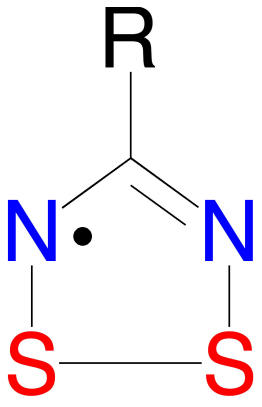


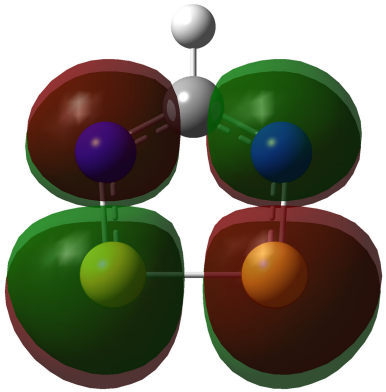
Preuss, *et al.*, *Chem. Commun.* **2012**, *46*, 10963.
Preuss, *et al.*, *Inorg. Chem.* **2021**, *60*, 11338.

Paramagnetic Group: DTDA

1,2,3,5-Dithiadiazolyl **Neutral Radical**



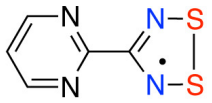
DTDA



SOMO

- Lone pair on N atoms, like pyridine
- No substituents on N & S atoms
- Supramolecular contacts…
  - Structure-directing?
  - Magnetism?
  - Conductivity?
  - Phase transition switching?

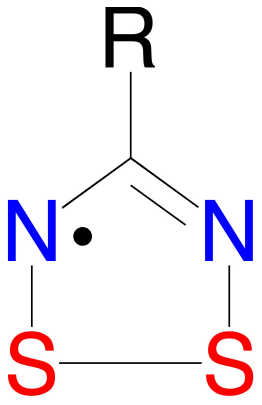
&

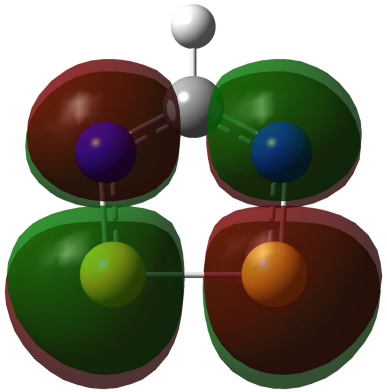


Preuss, *et al., J. Am. Chem. Soc.* **2004**, *126*, 9942.
Preuss, *et al.*, *Chem. Commun.* **2006**, 341.

1,2,3,5-DTDA Synthesis

1,2,3,5-Dithiadiazolyl **Neutral Radical**





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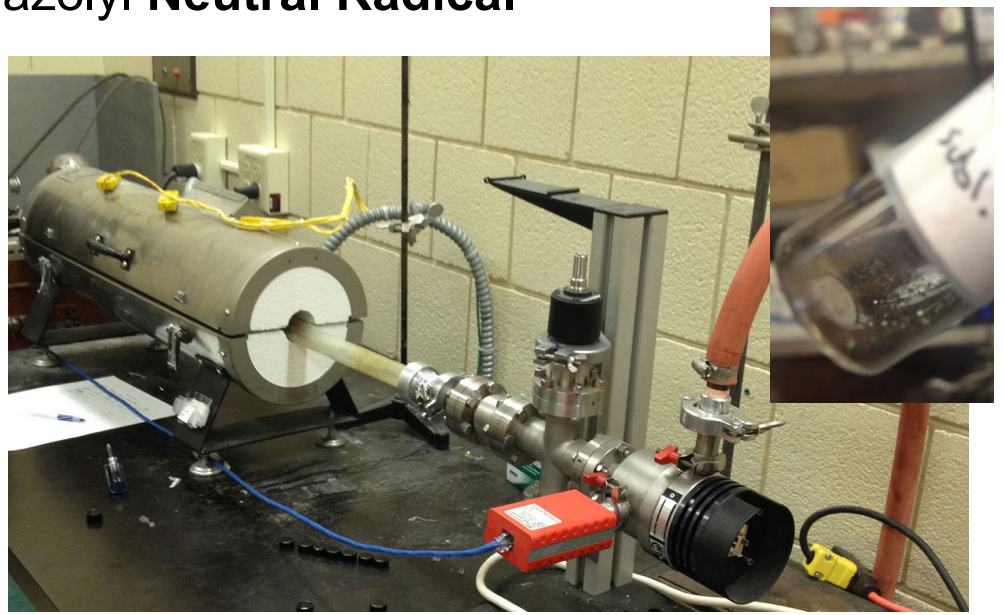

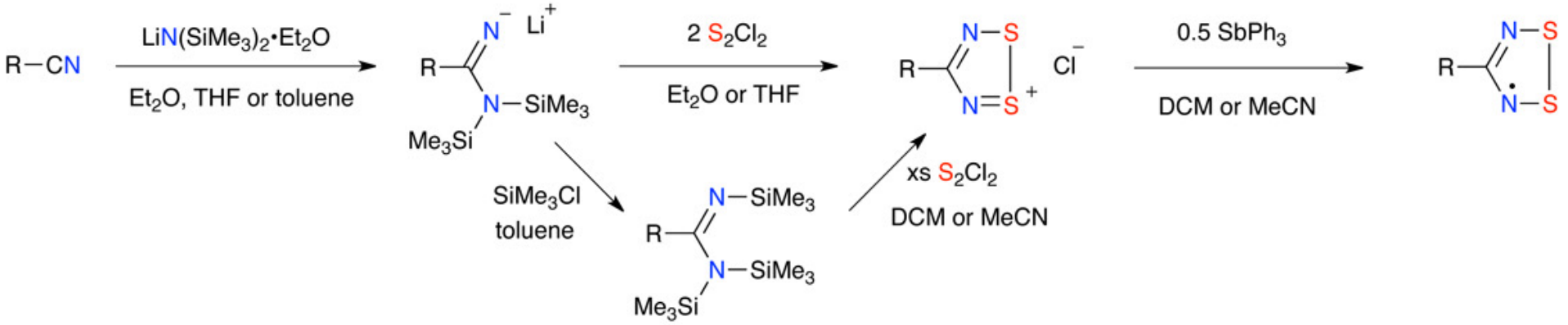

Boere, Oakley & Reed, *J. Organomet. Chem.* **1987**, *331*, 161.
Oakley, *et al.*, *J. Am. Chem. Soc.* **1989**, *111*, 9276.
Rawson, *et al.*, *CrystEngComm*, **2013**, *15*, 1107.

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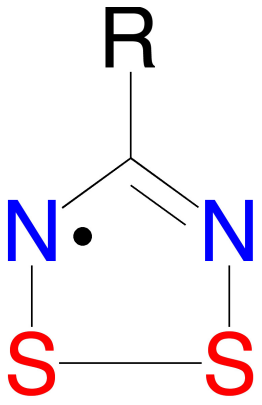
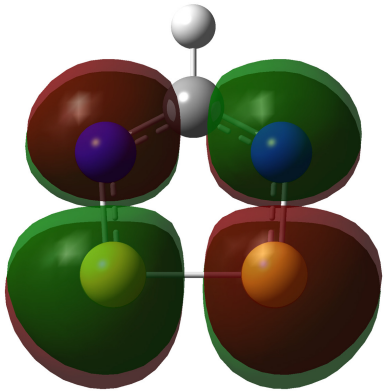
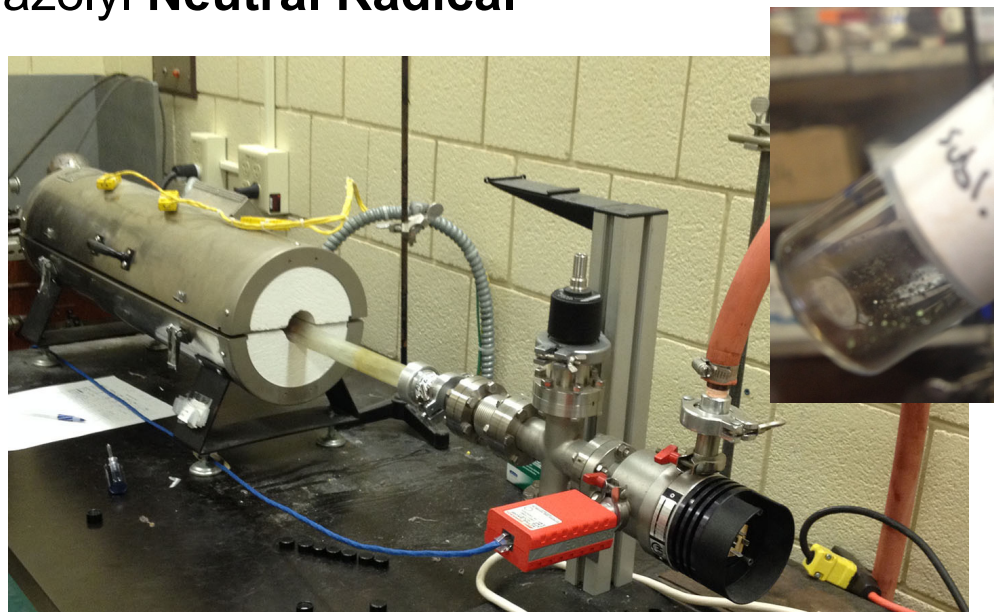
1,2,3,5-DTDA: ligand design

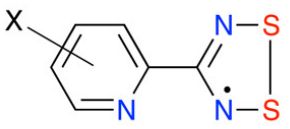
1,2,3,5-Dithiadiazolyl **Neutral Radical**



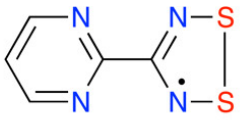


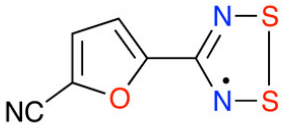
SOMO

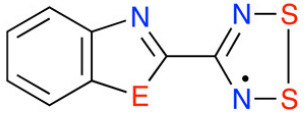




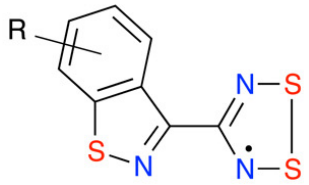
X = H, F, Br, CN,...







E = O, S



R = H, Me

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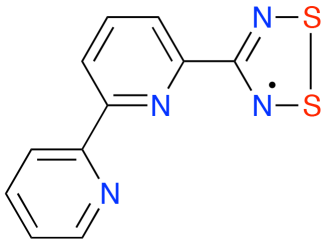
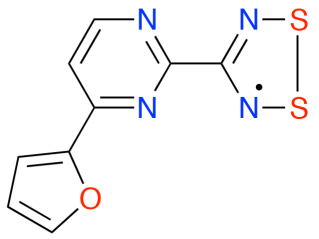
Chem. Commun. **2006**, 341.
Inorg. Chem. **2007**, *46*, 3934.
Polyhedron. **2007**, *26*, 2047.

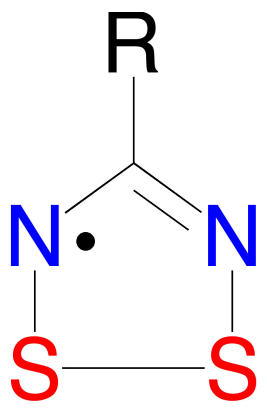
Inorg. Chem. **2008**, *47*, 10330.
Dalton Trans. **2009**, 3192.
Chem. Commun. **2010**, 6569.
Inorg. Chem. **2012**, *51*, 3827.

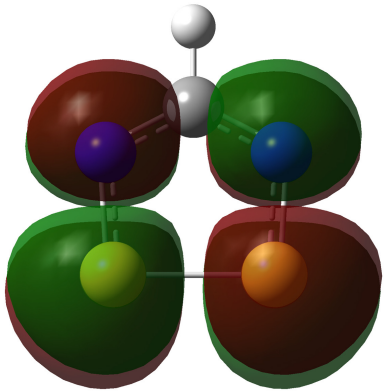




FM Coupling: Ni^{II}-Rad-Ni^{II}

1,2,3,5-Dithiadiazolyl **Neutral Radical**





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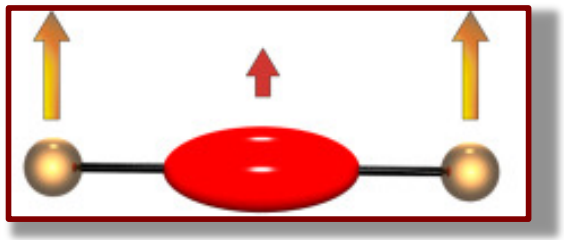
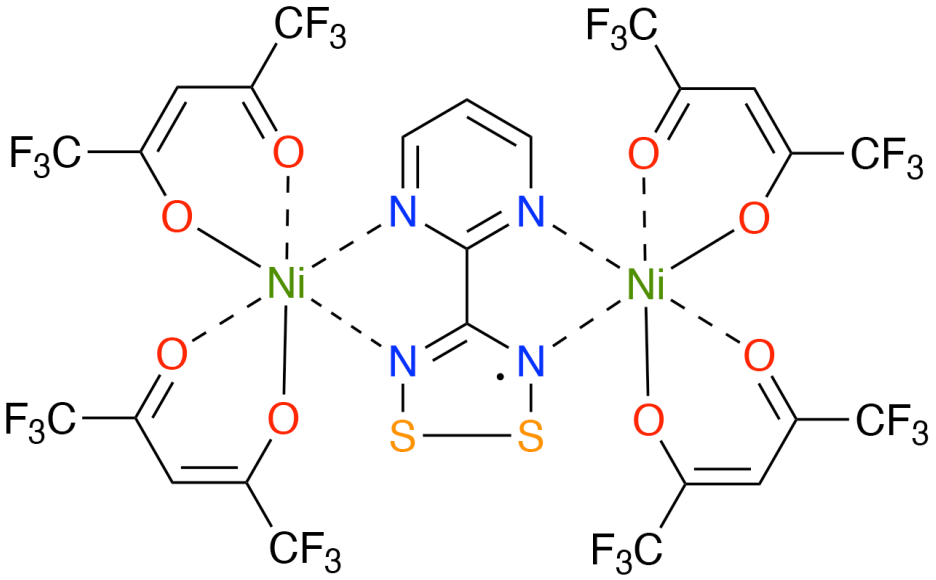
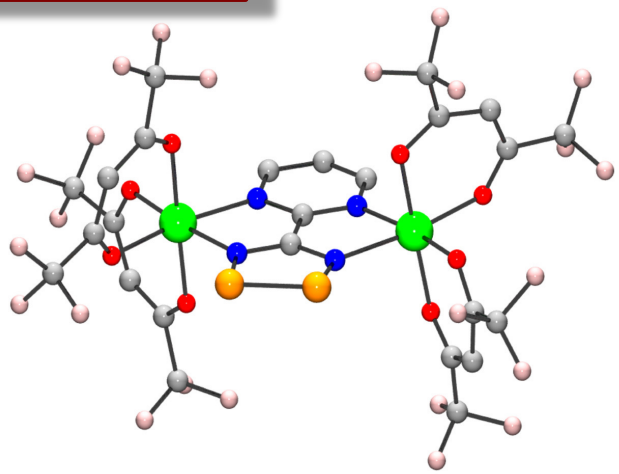




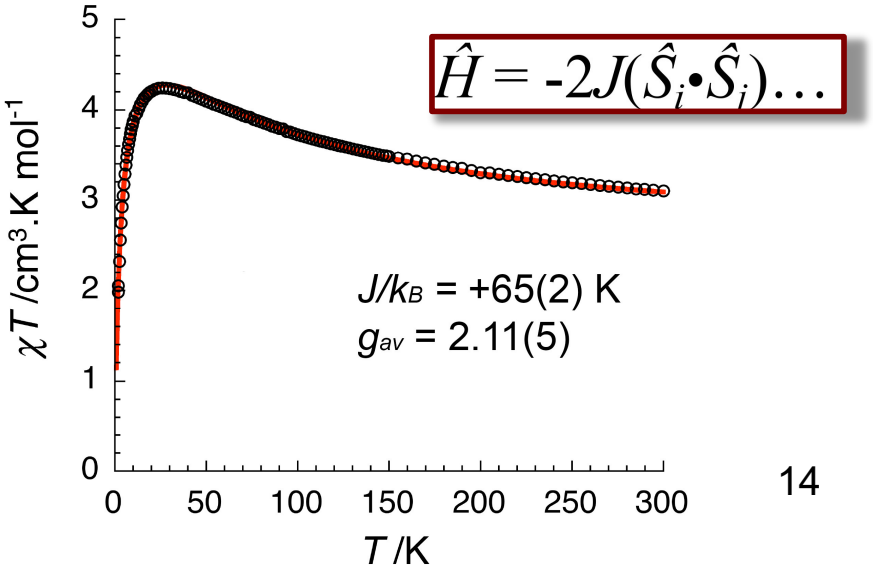
d^8

FM



Ni(II) complex $S_T = 5/2$

Preuss, *et al.*, *Inorg. Chem.* **2012**, *51*, 3827.



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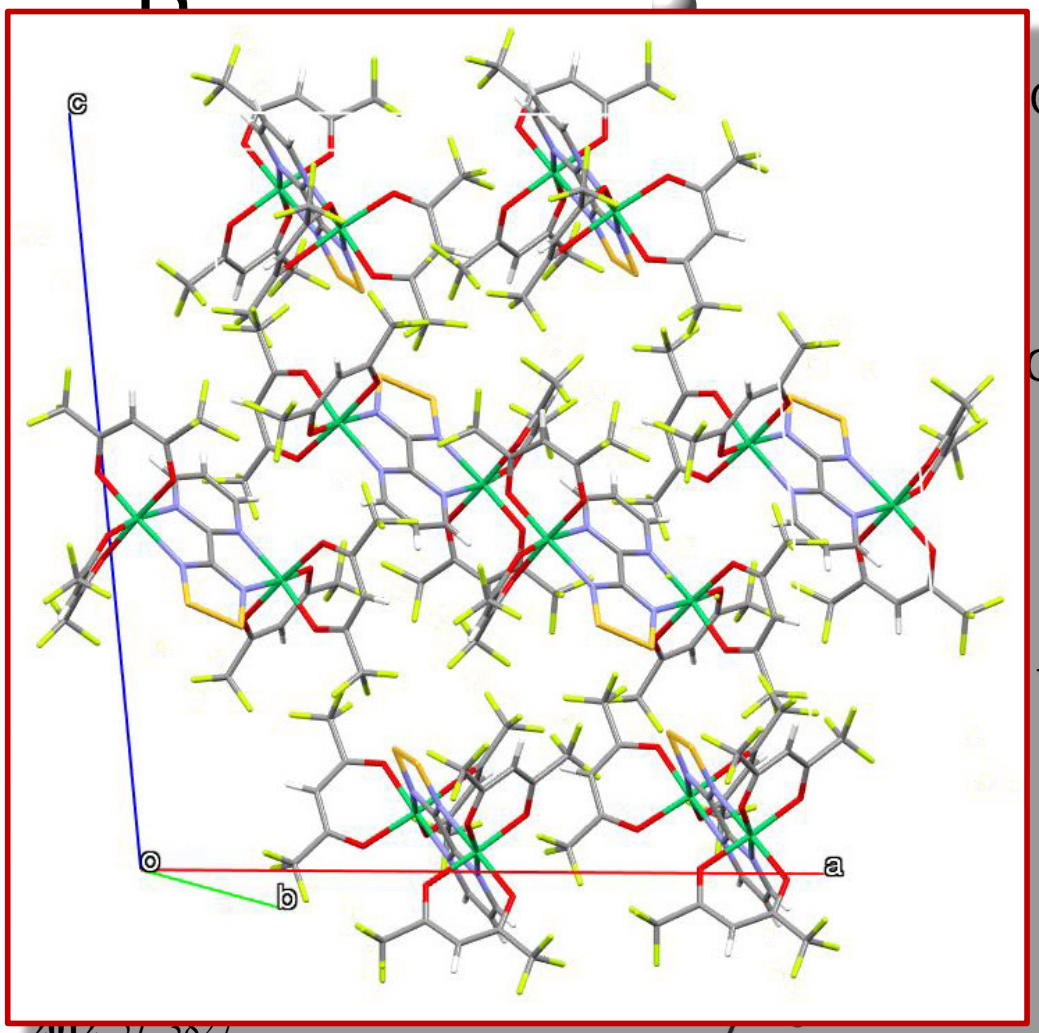
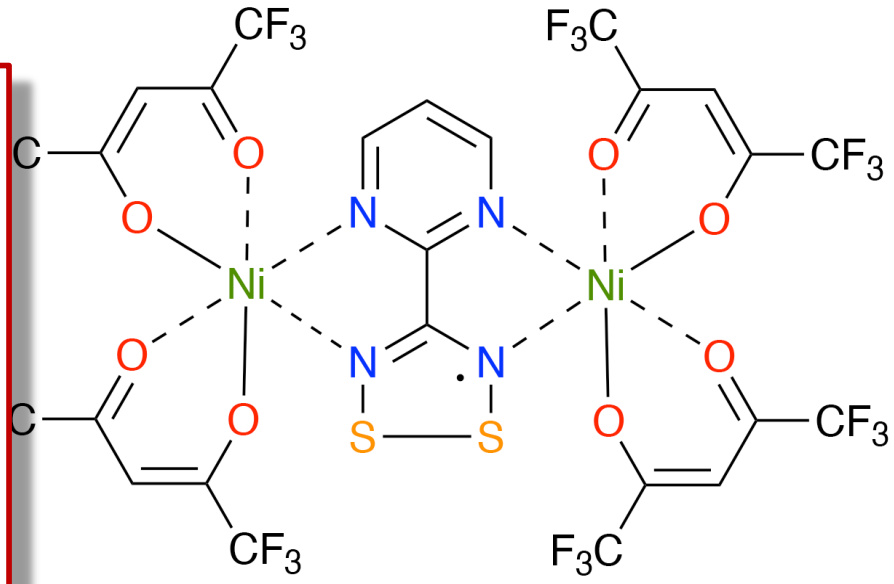
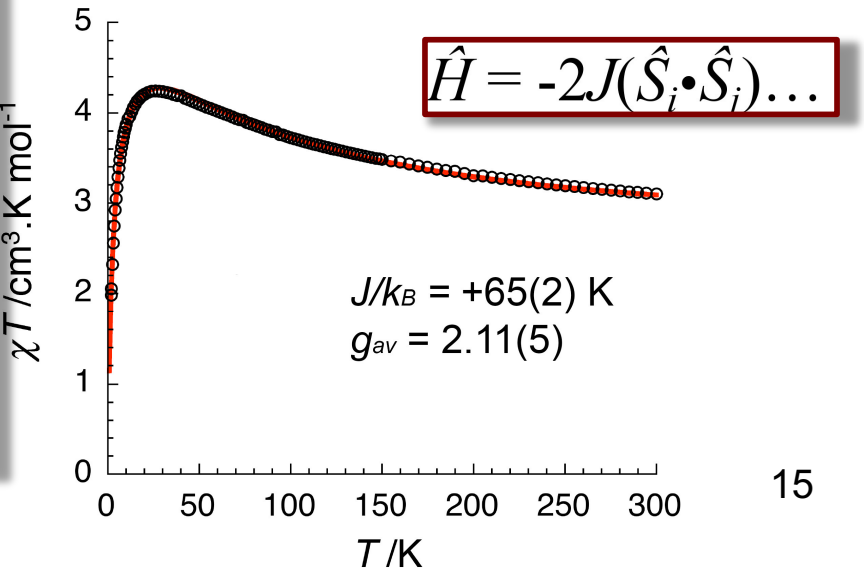
FM Coupling: Ni^{II}-Rad-Ni^{II}

1,2,3,5-Dithiadiazolyl **Neutral Radical**





Ni(II) complex $S_T = 5/2$



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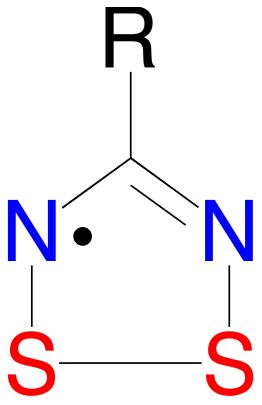
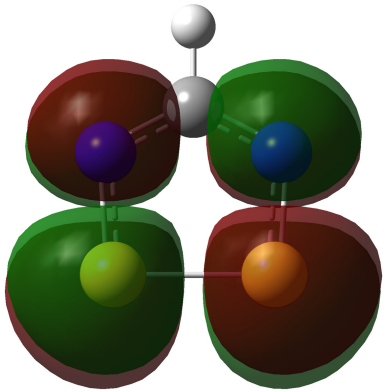
1,2,3,5-DTDA: ligand design

1,2,3,5-Dithiadiazolyl **Neutral Radical**





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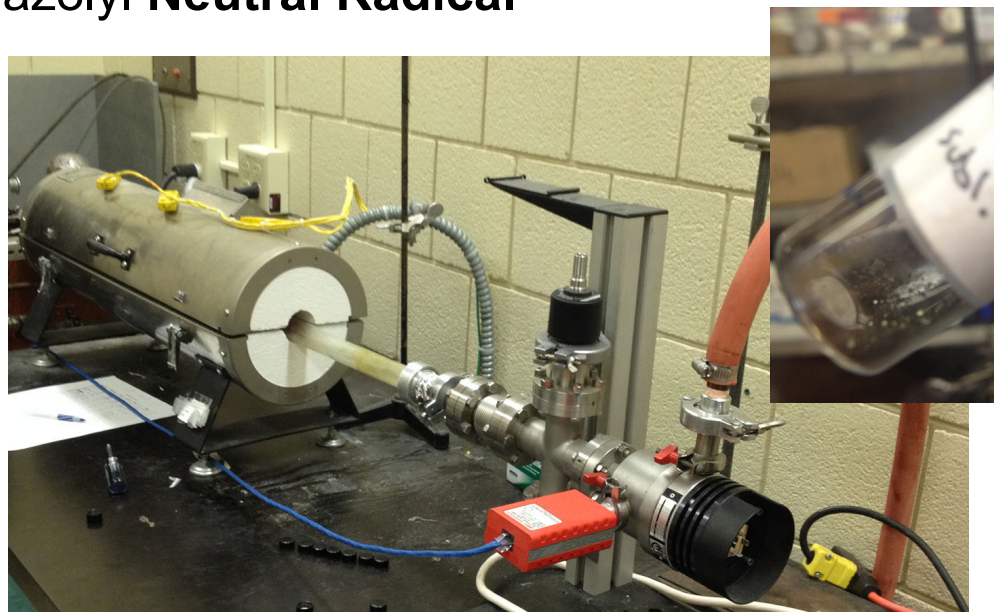
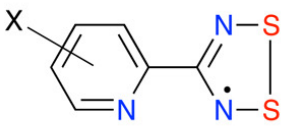
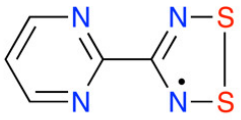
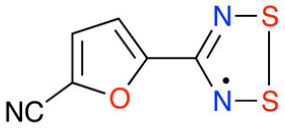
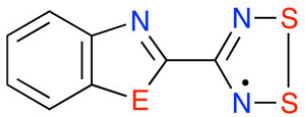




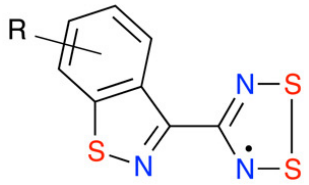
X = H, F, Br, CN,...



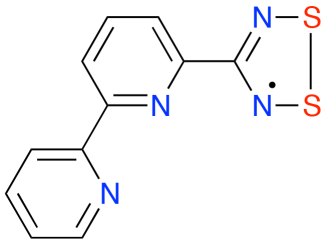


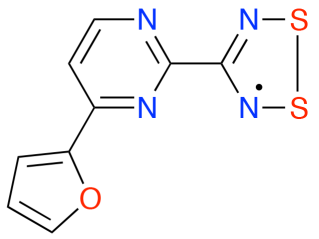


E = O, S



R = H, Me



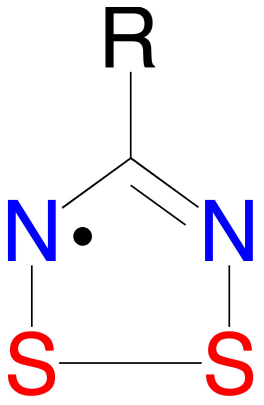


J. Am. Chem. Soc. **2004**, *126*, 9942.
Chem. Commun. **2006**, 341.
Inorg. Chem. **2007**, *46*, 3934.
Polyhedron. **2007**, *26*, 2047.

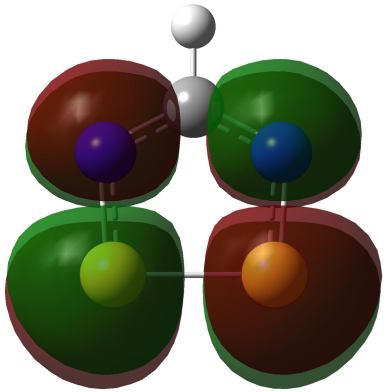
Inorg. Chem. **2008**, *47*, 10330.
Dalton Trans. **2009**, 3192.
Chem. Commun. **2010**, 6569.
Inorg. Chem. **2012**, *51*, 3827.

Paramagnetic Group: DTDA

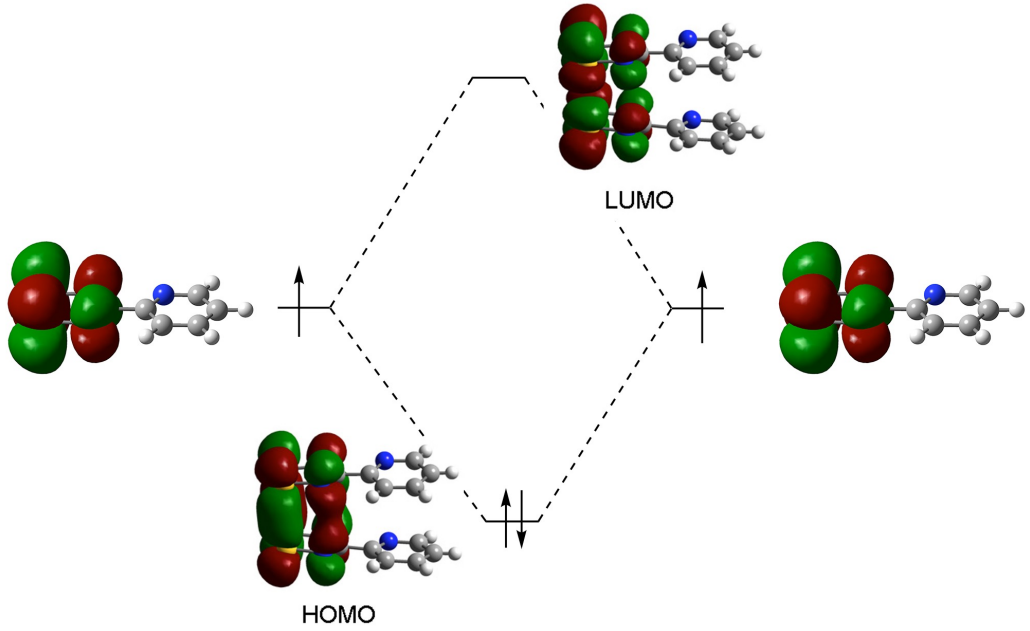
Pair-wise co-facial association of planar π–radicals



1,2,3,5-Dithiadiazolyl
(DTDA)



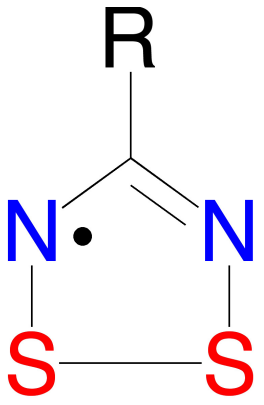
SOMO



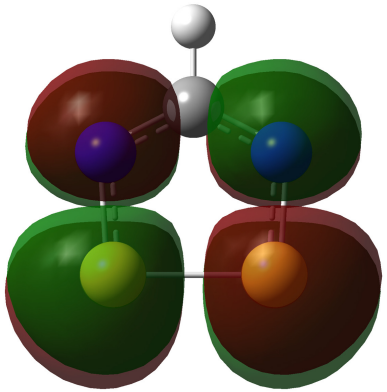
- mc/2e bond

Pancake Bond

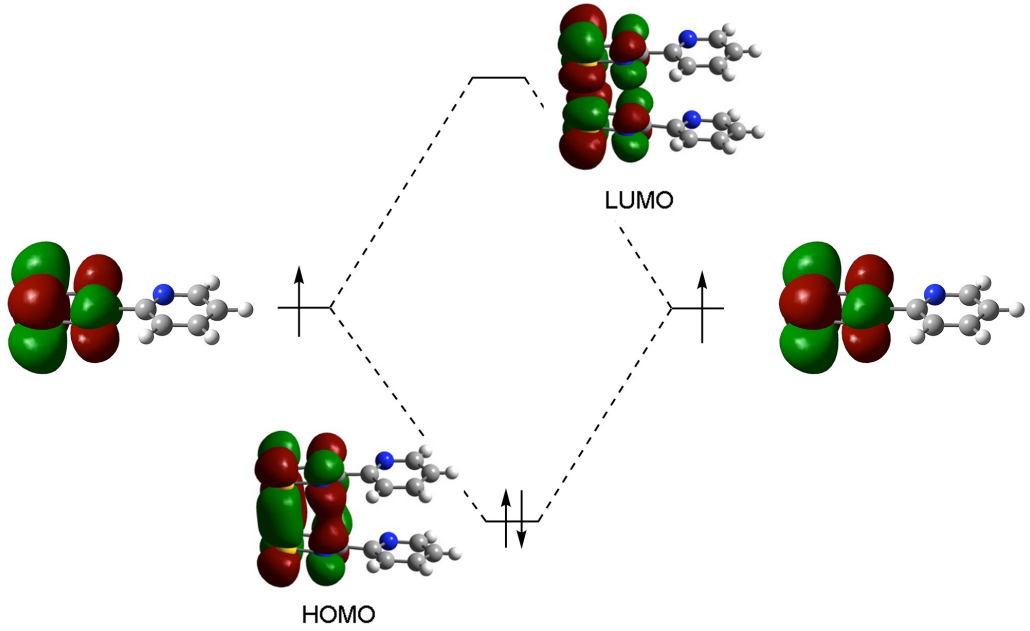
Pair-wise co-facial association of planar π–radicals



1,2,3,5-Dithiadiazolyl
(DTDA)



SOMO

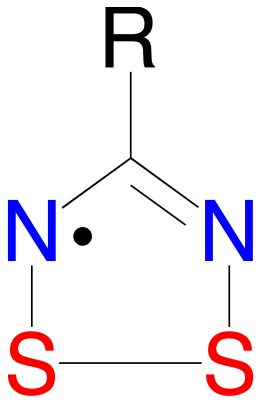


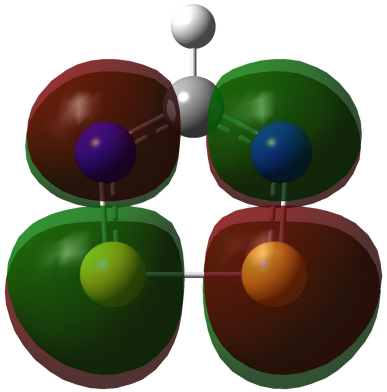
- mc/2e bond

PANCAKE BOND

Pancake Bond

Pair-wise co-facial association of planar π–radicals





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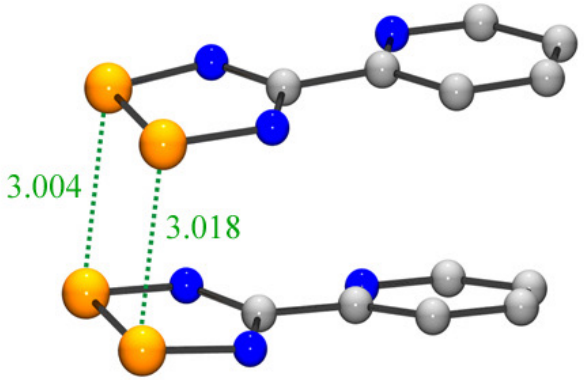
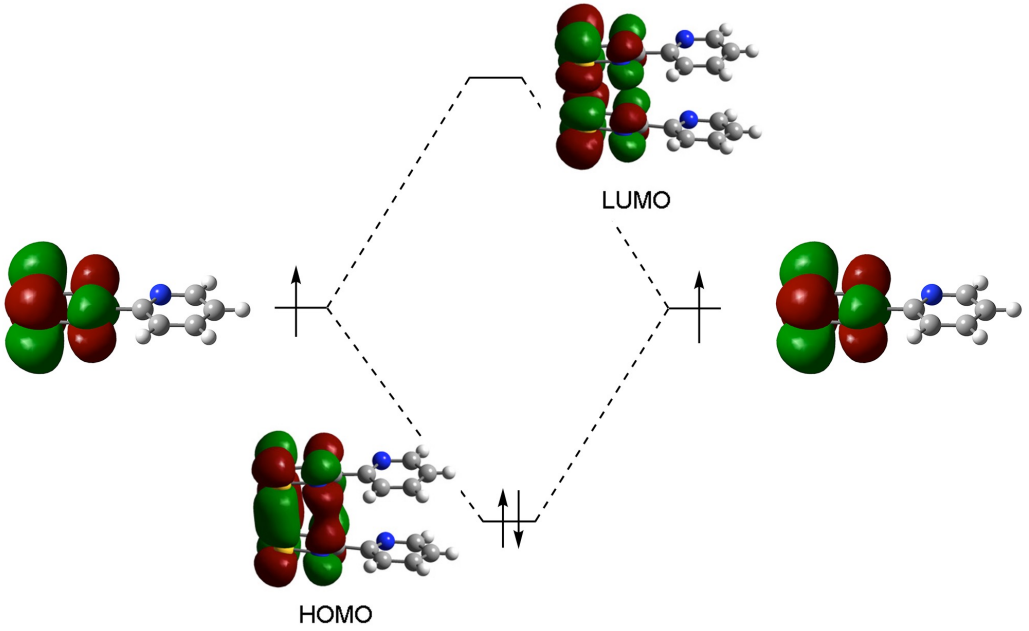
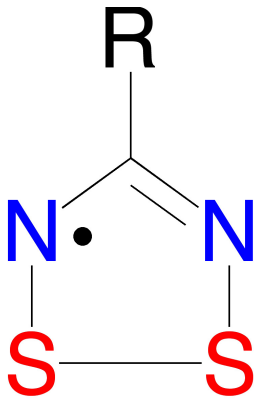


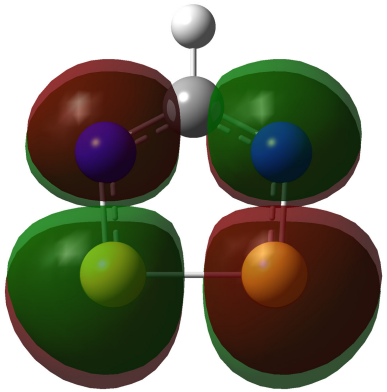


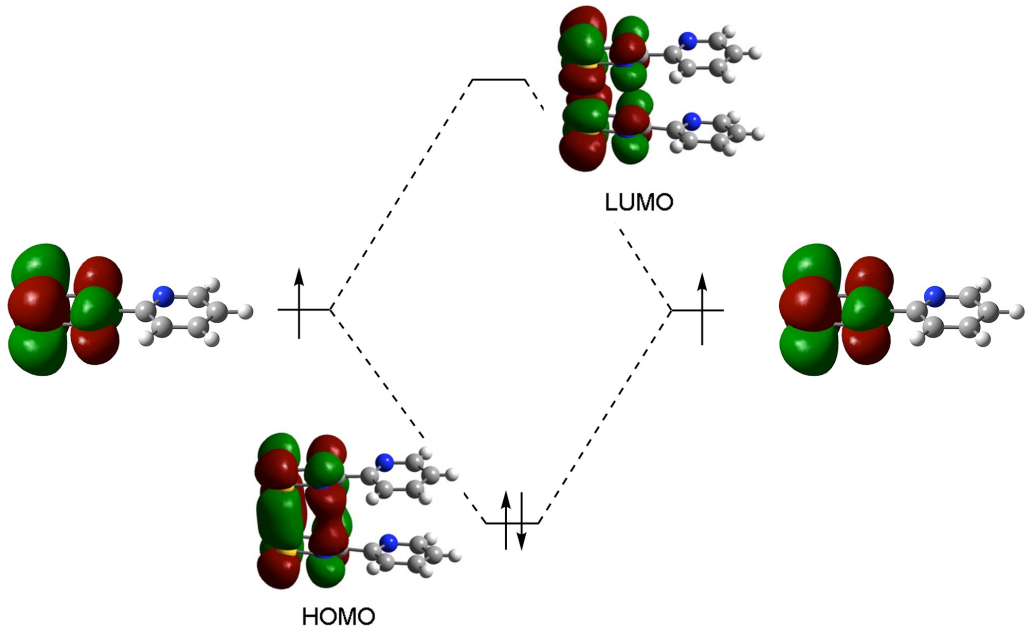
- mc/2e bond
- Intermolecular distances *shorter* than sum of v.d.W.r.

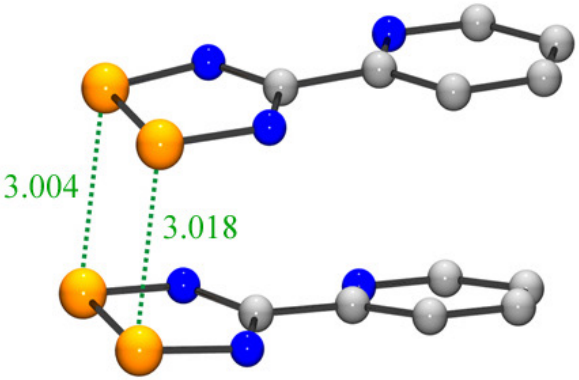
Pancake Bond

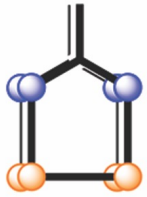
Pair-wise co-facial association of planar π–radicals

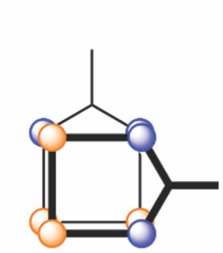


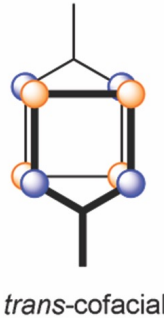


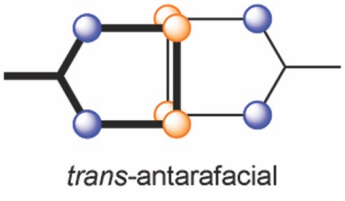












- mc/2e bond
- Intermolecular distances *shorter* than sum of v.d.W.r.
- Stringent Geometric Requirement

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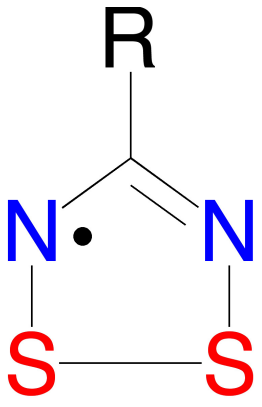
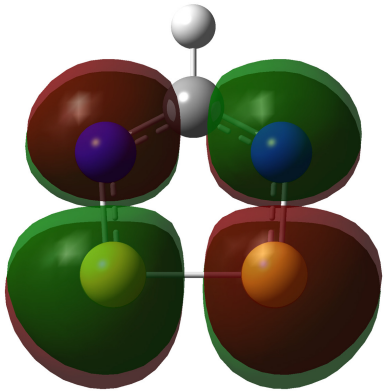
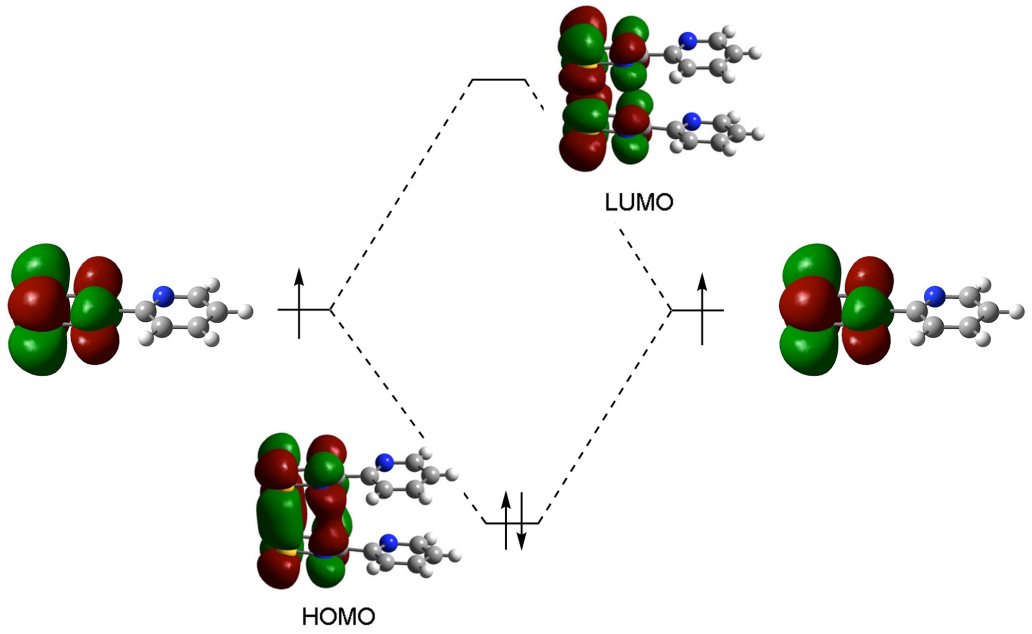
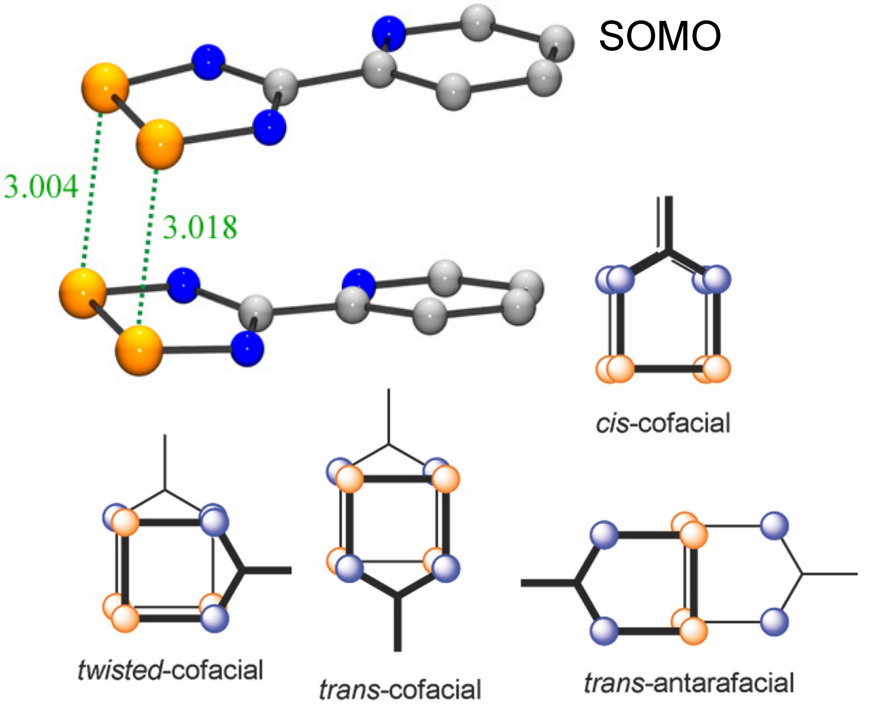
1,2,3,5-DTDA Pancake Bonding

Pair-wise co-facial association of planar π–radicals









DIAMAGNETIC

"pancake bonds"
or
π–π dimers

Pancake Bond Enthalpy
~ 35 kJ/mol

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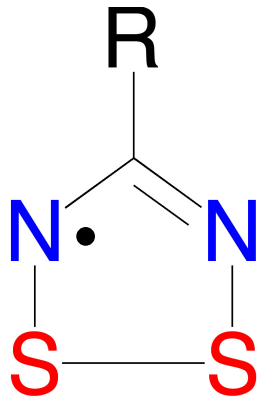
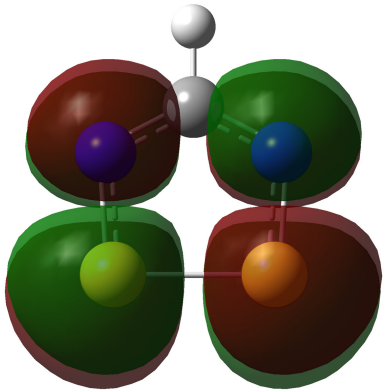
1,2,3,5-DTDA Pancake Bonding

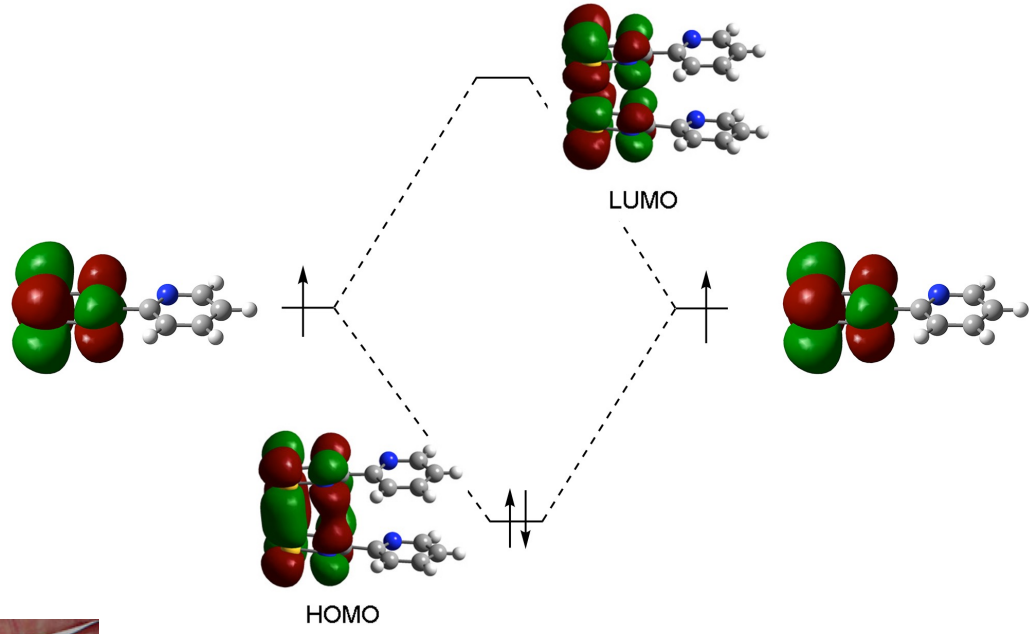
Pair-wise co-facial association of planar π–radicals



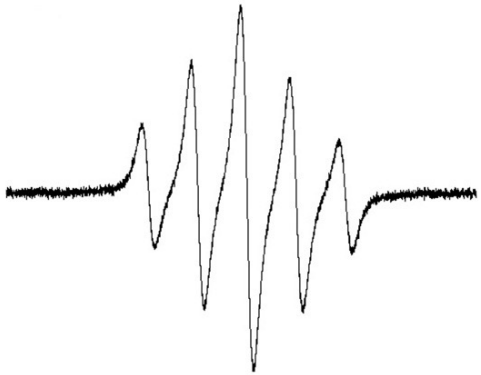
1,2,3,5-Dithiadiazolyl
(DTDA)



SOMO



EPR in CH_2Cl_2 @ RT



$g = 2.010(6)$
$a_N = 5.02$ G

PARAMAGNETIC

In dilute solution,
MONOMERS

RT

Preuss, *et al., Inorg. Chem.* **2007**, *46*, 3934.

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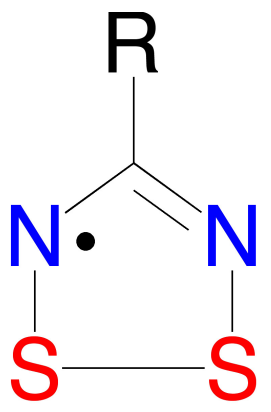
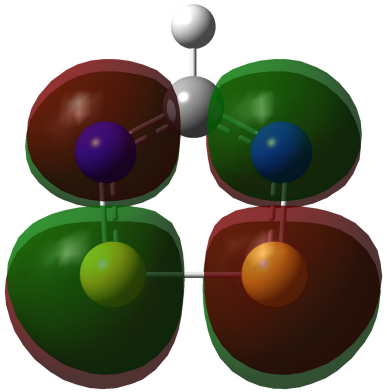
1,2,3,5-DTDA Pancake Bonding

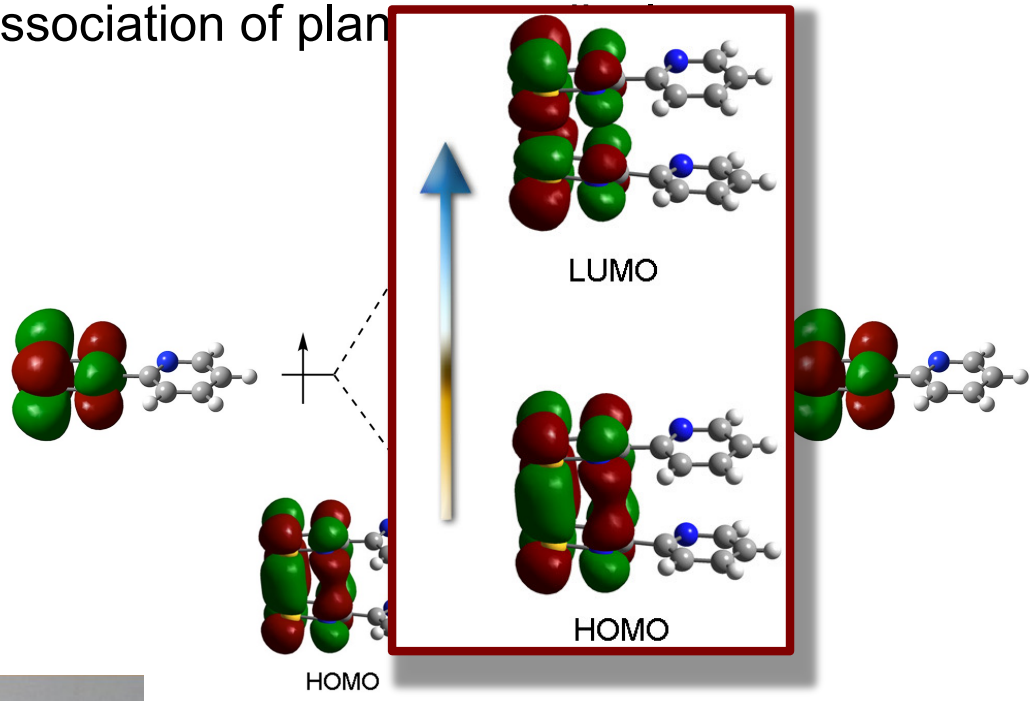
Pair-wise co-facial association of plan

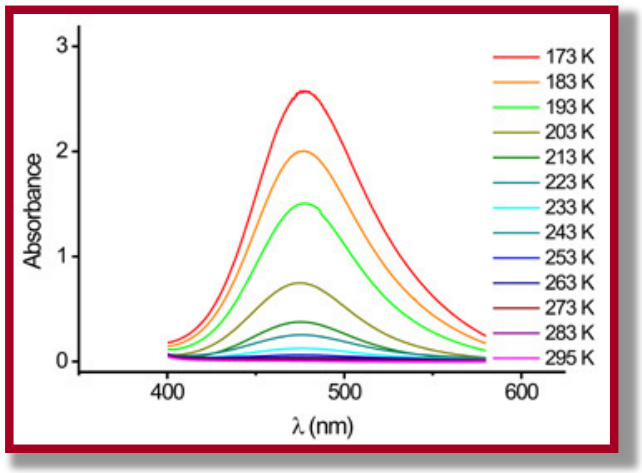


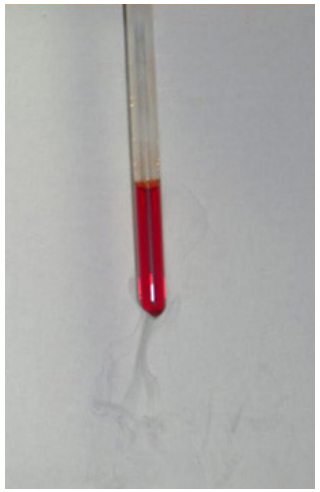
1,2,3,5-Dithiadiazolyl
(DTDA)



SOMO





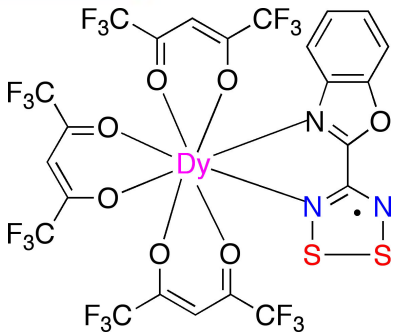


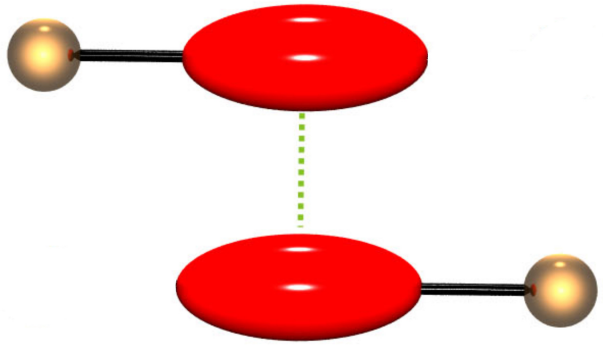
DIAMAGNETIC
DIMERS
In dilute solution
LT

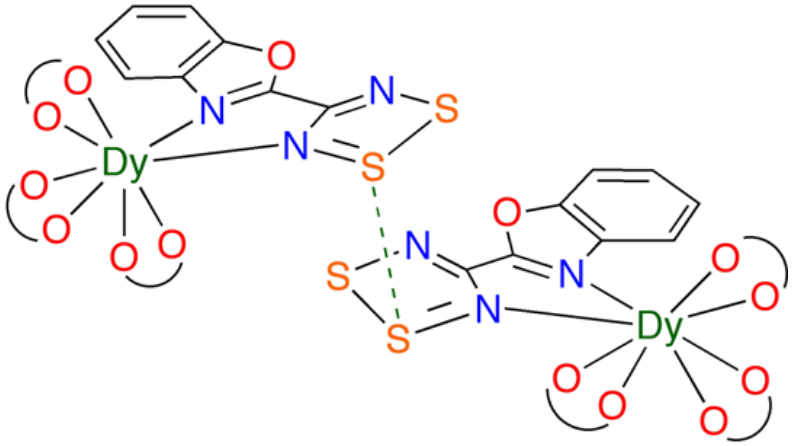
Pancake bonds
reformed

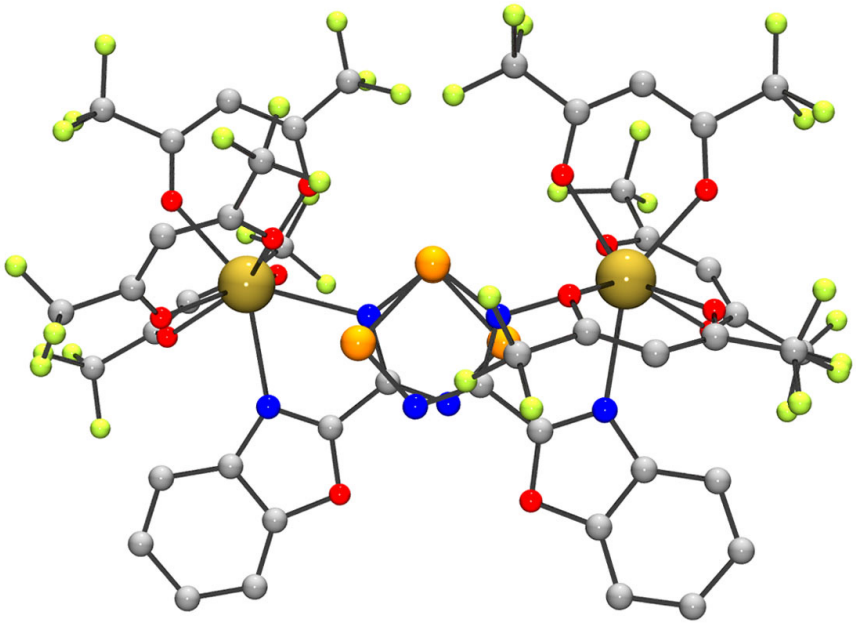
Preuss, *et al., Inorg. Chem.* **2007**, *46*, 3934.

boaDTDA - Dy(III) dimers



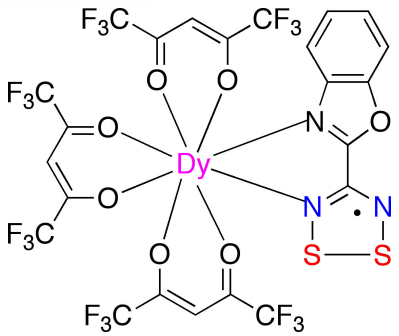


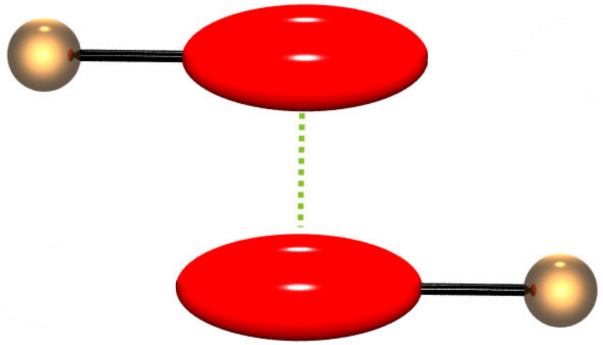


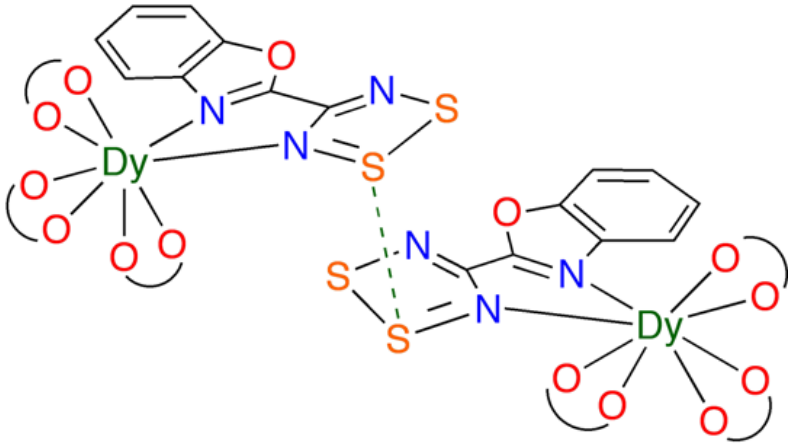


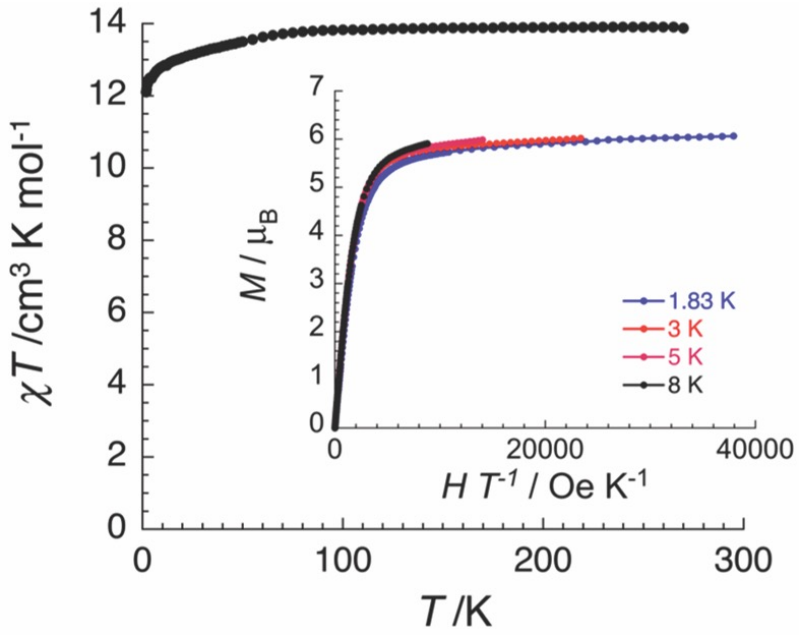
E. M. Fatila, M. Rouzières, M. C. Jennings, A. J. Lough, R. Clérac, K. Preuss, *J. Am. Chem. Soc.* **2013**, *135*, 9596.

boaDTDA - Dy(III) dimers

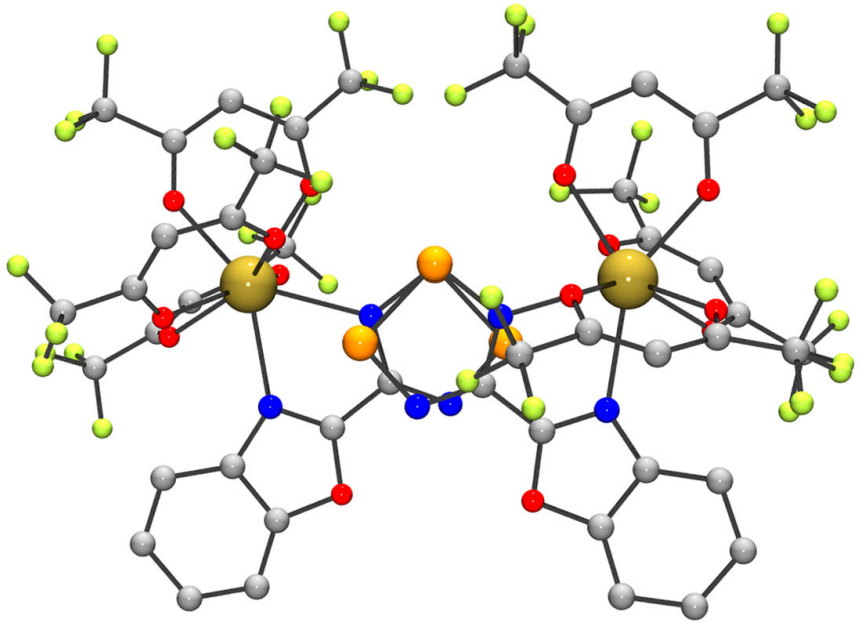








$[DTDA]_2$ unit is diamagnetic



E. M. Fatila, M. Rouzières, M. C. Jennings, A. J. Lough, R. Clérac, K. Preuss, *J. Am. Chem. Soc.* **2013**, *135*, 9596.

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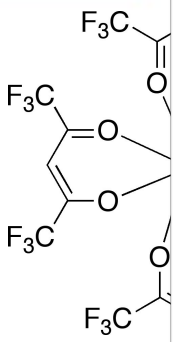

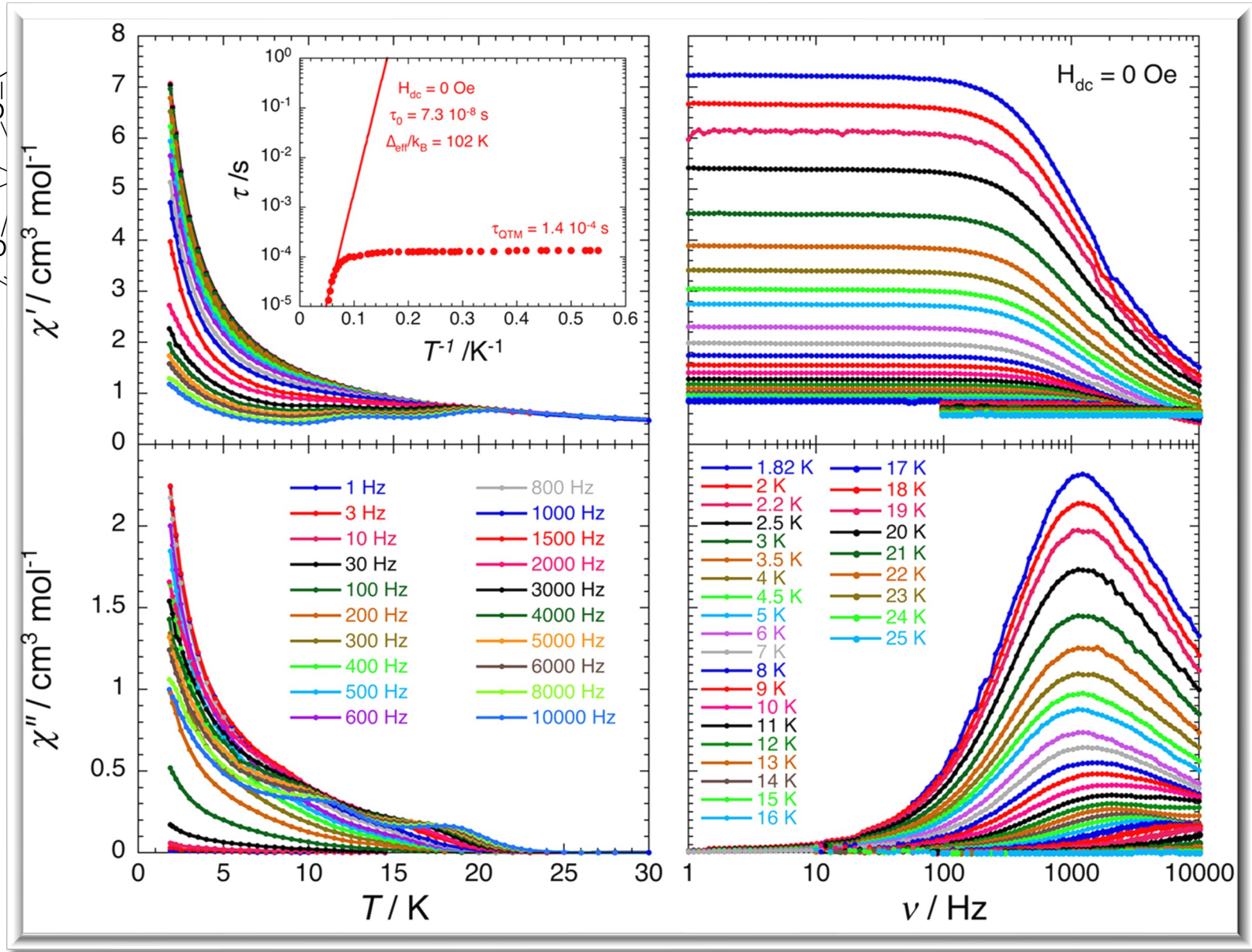

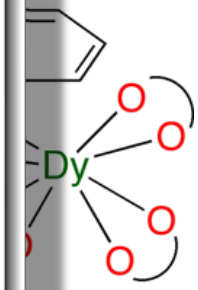

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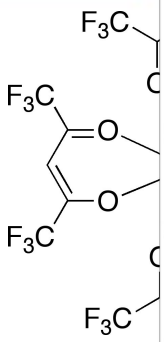
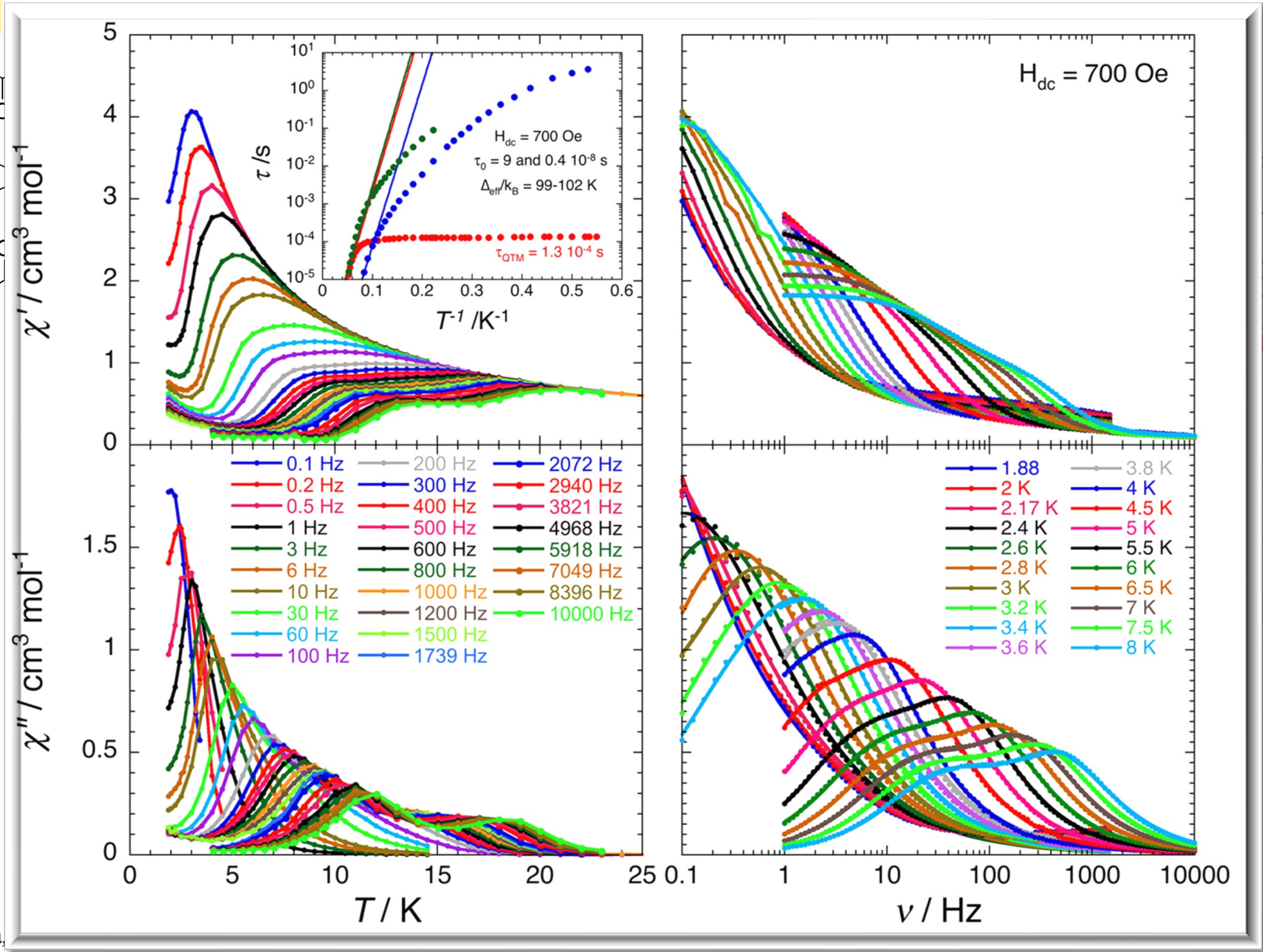
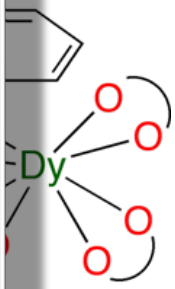
boaDTDA - Dy(III) dimers







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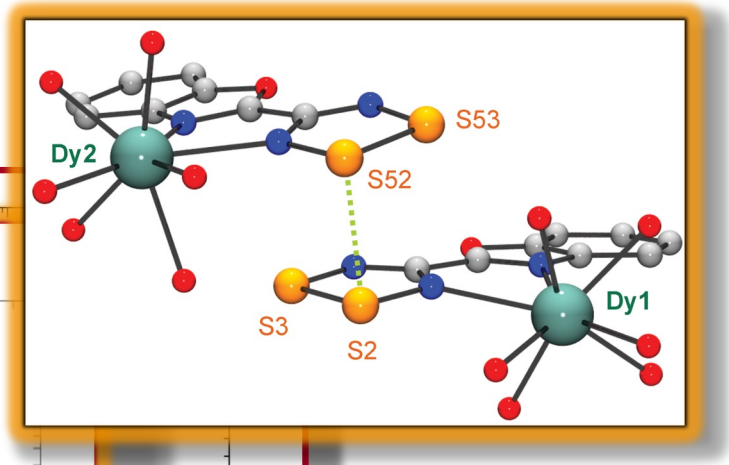
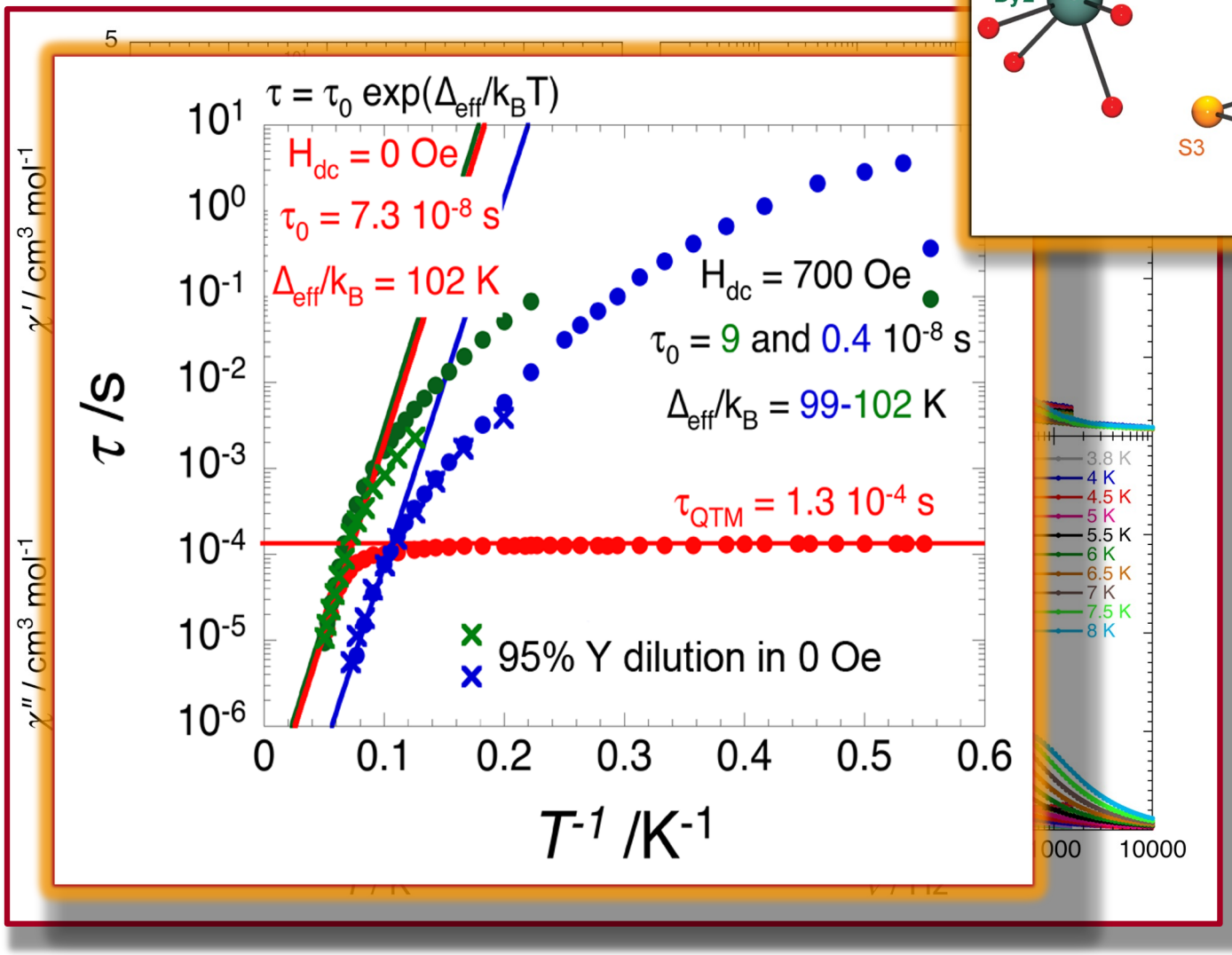
boaDTDA - Dy(III) dimers





5% Dy in 95% Y

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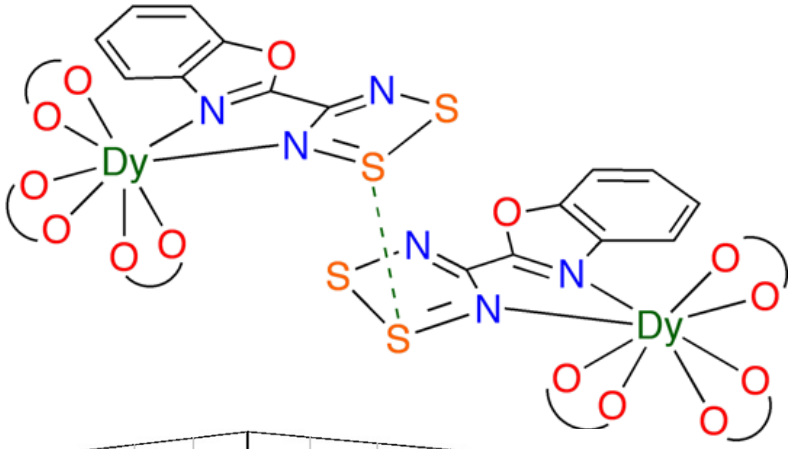
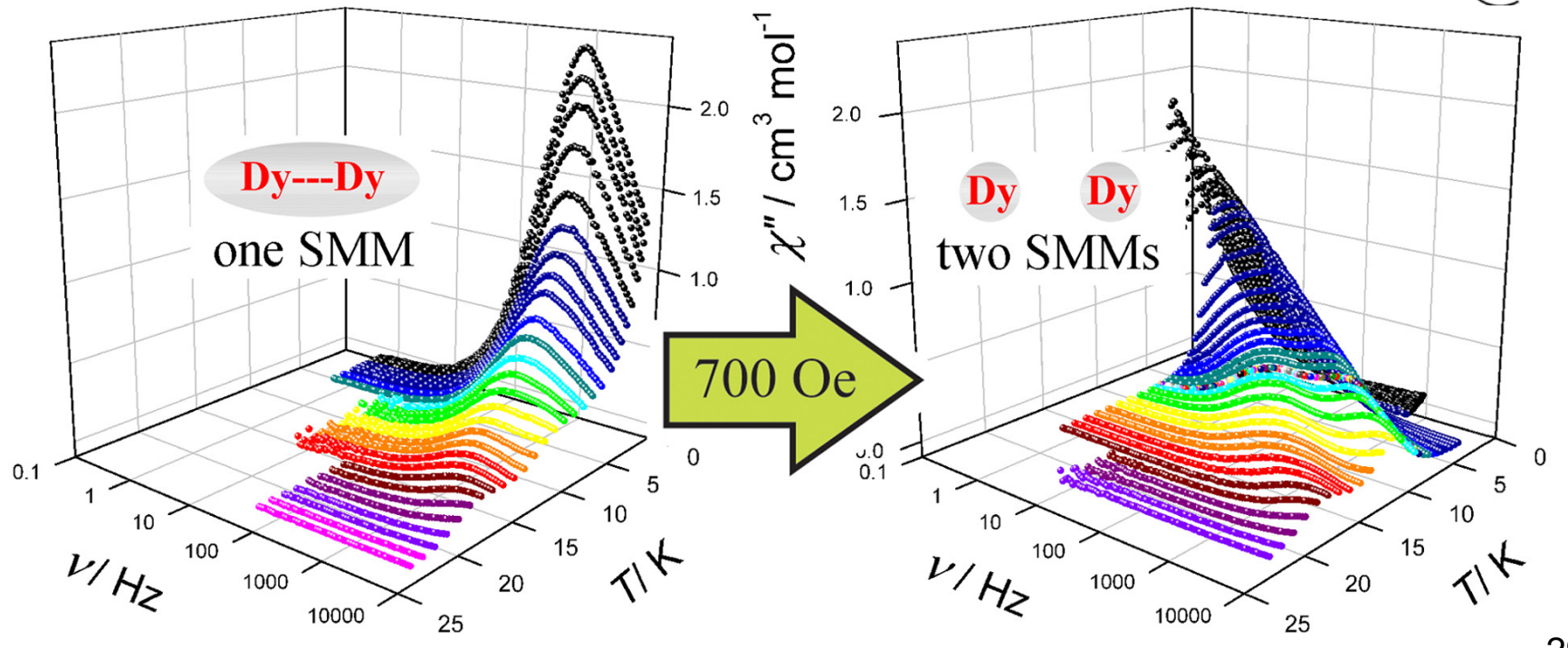
boaDTDA - Dy(III) dimers

Dy(III) ions are crystallographically unique

Weakly AF coupled!





E. M. Fatila, M. Rouzières, M. C. Jennings, A. J. Lough, R. Clérac, K. Preuss, *J. Am. Chem. Soc.* **2013**, *135*, 9596.

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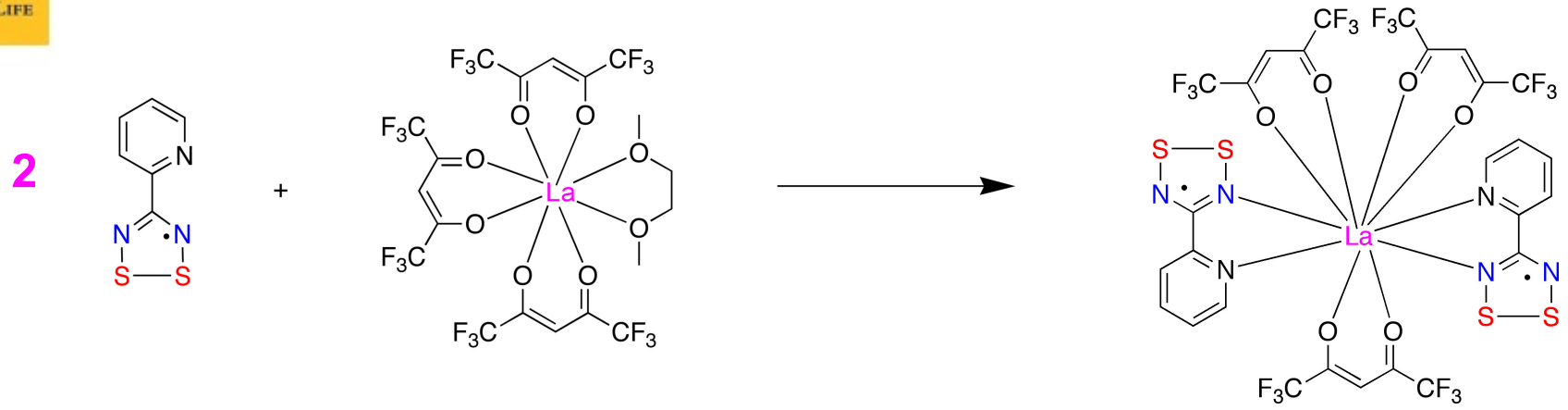
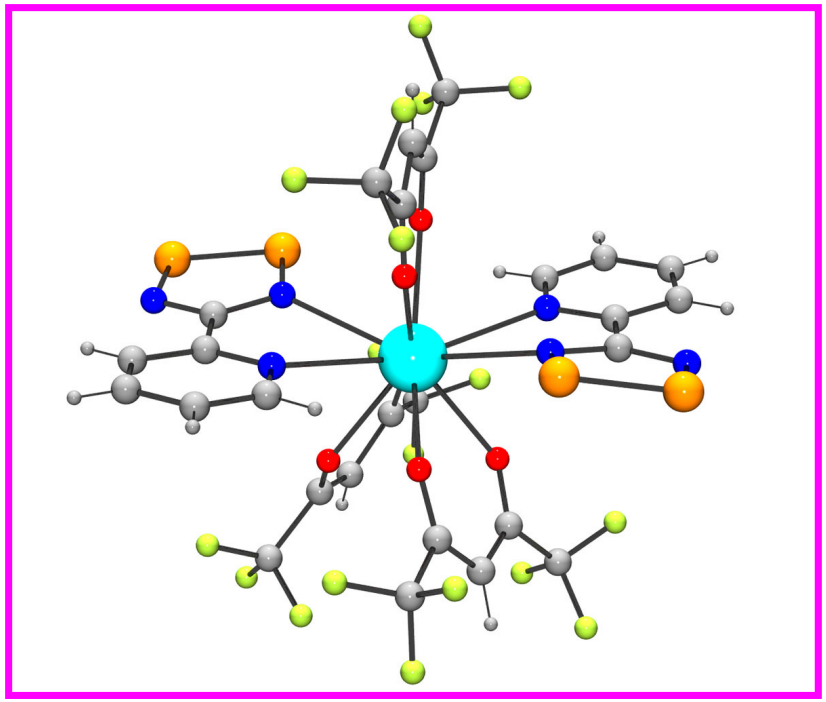
Re-entrant Phase Transition





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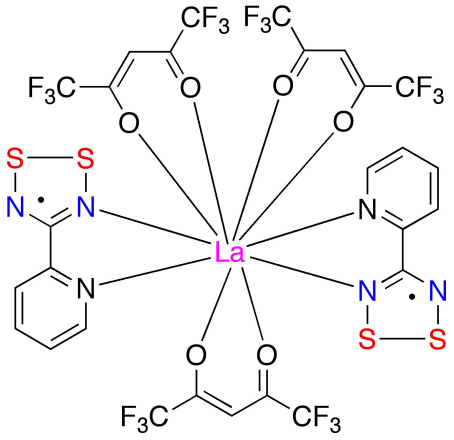
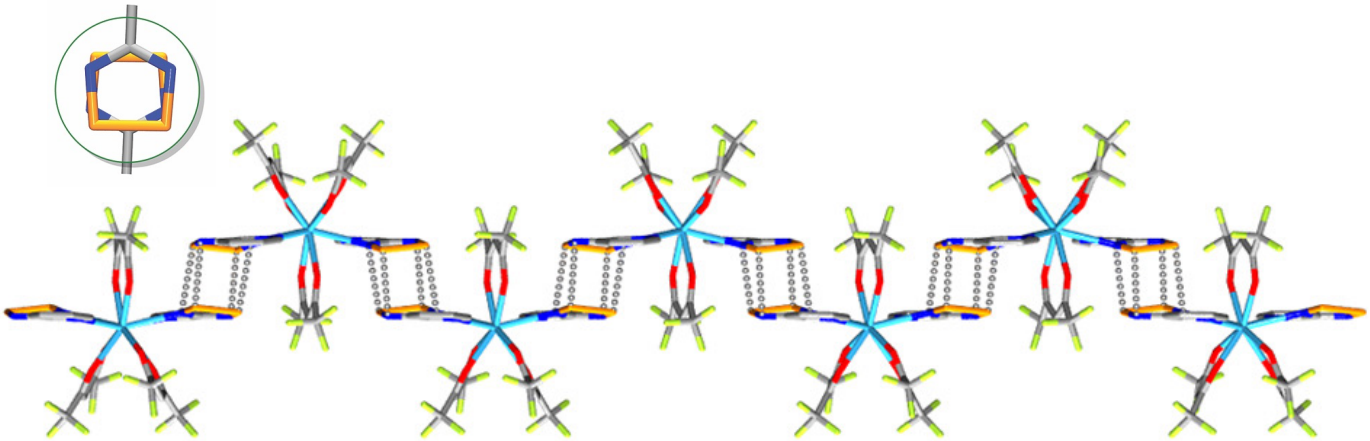
Re-entrant Phase Transition





Preuss, Clérac, Coulon, *et al*. *Chem. Mater.*. **2015**, DOI: 10.1021/acs.chemmater.5b00967.

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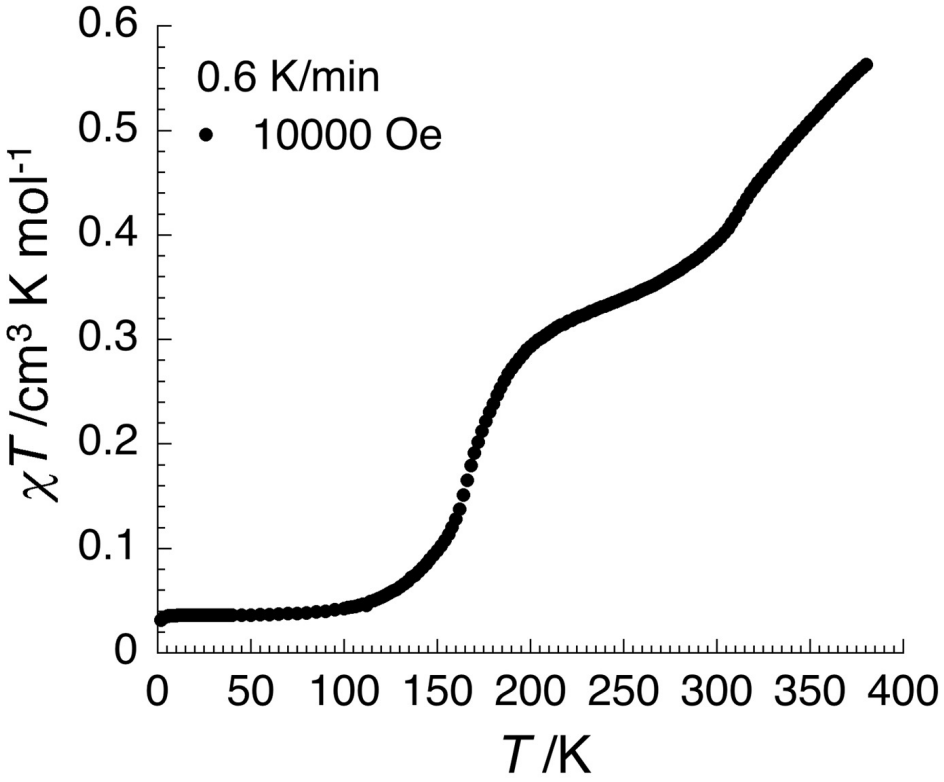
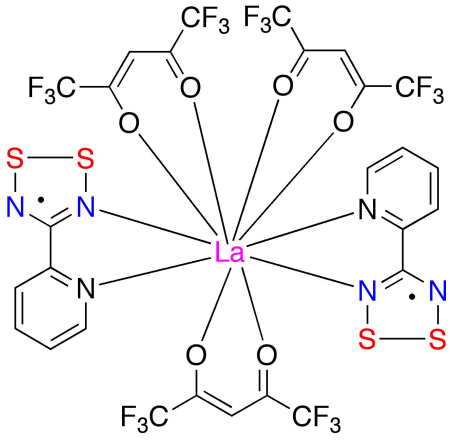
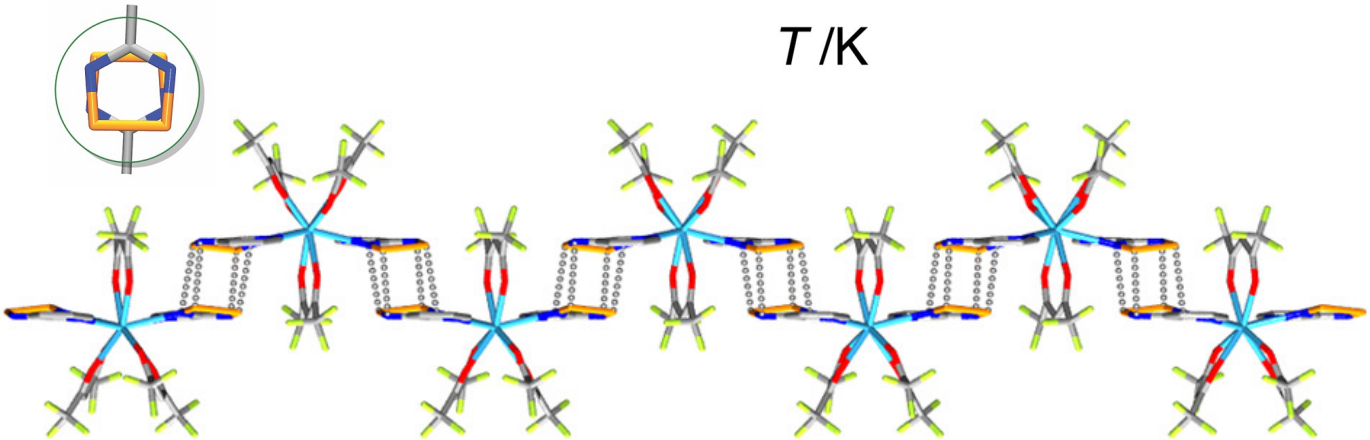
Re-entrant Phase Transition

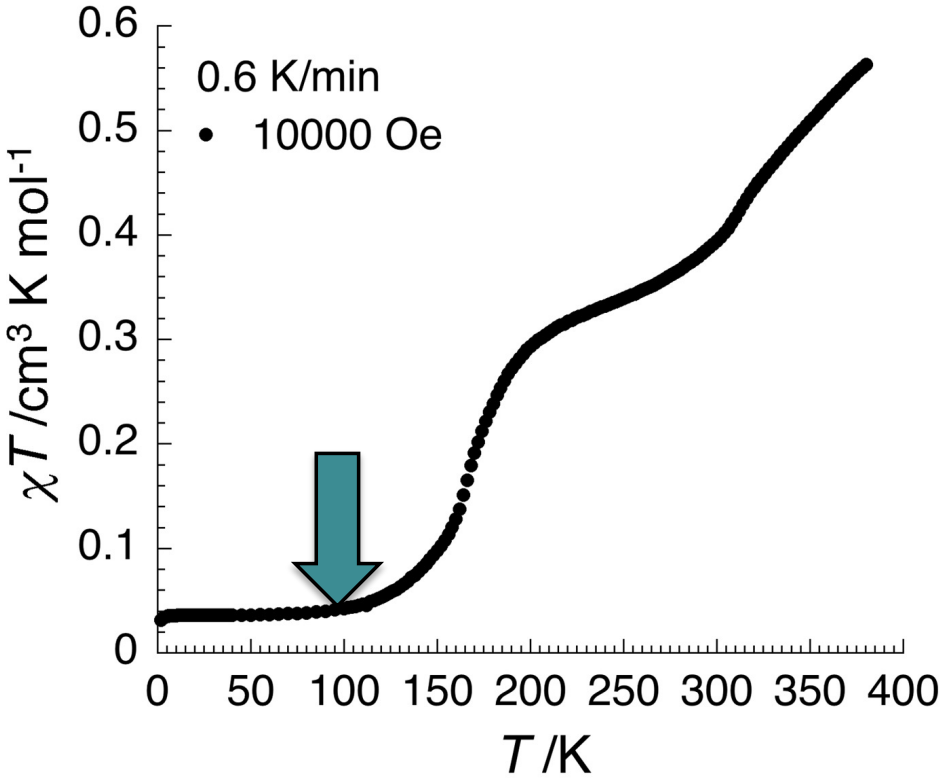


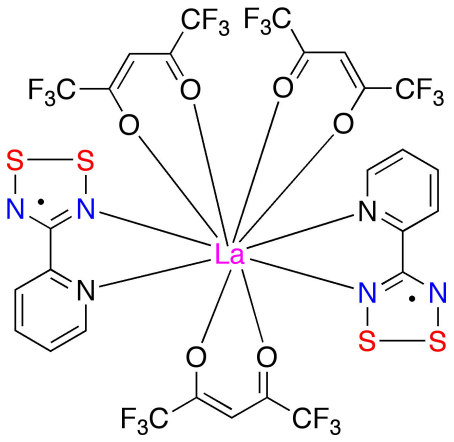


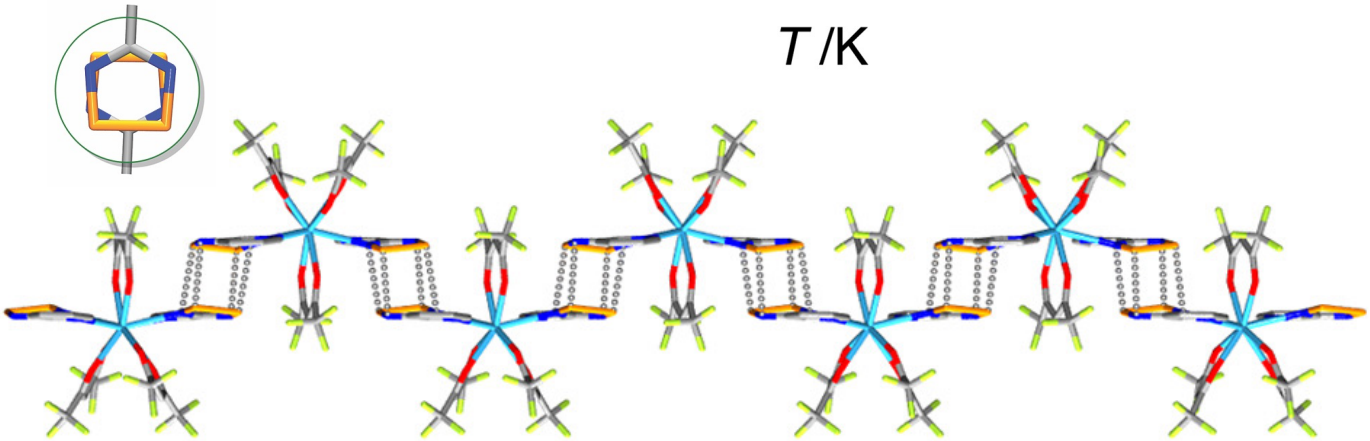


Preuss, Clérac, Coulon, *et al*. *Chem. Mater.*. **2015**, DOI: 10.1021/acs.chemmater.5b00967.

Re-entrant Phase Transition







*C*2/*c*

100 K

Preuss, Clérac, Coulon, *et al*. *Chem. Mater*.. **2015**, DOI: 10.1021/acs.chemmater.5b00967.

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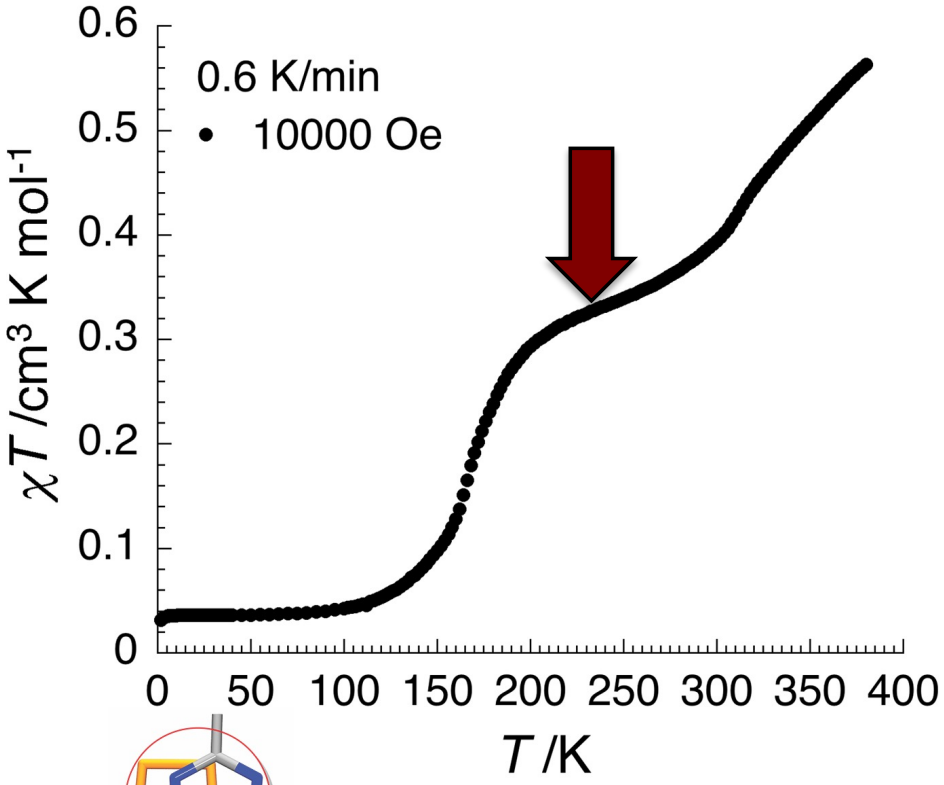
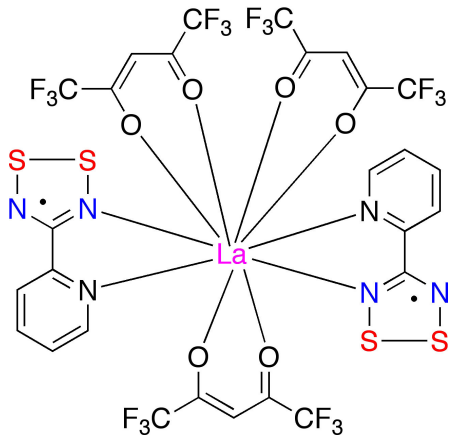
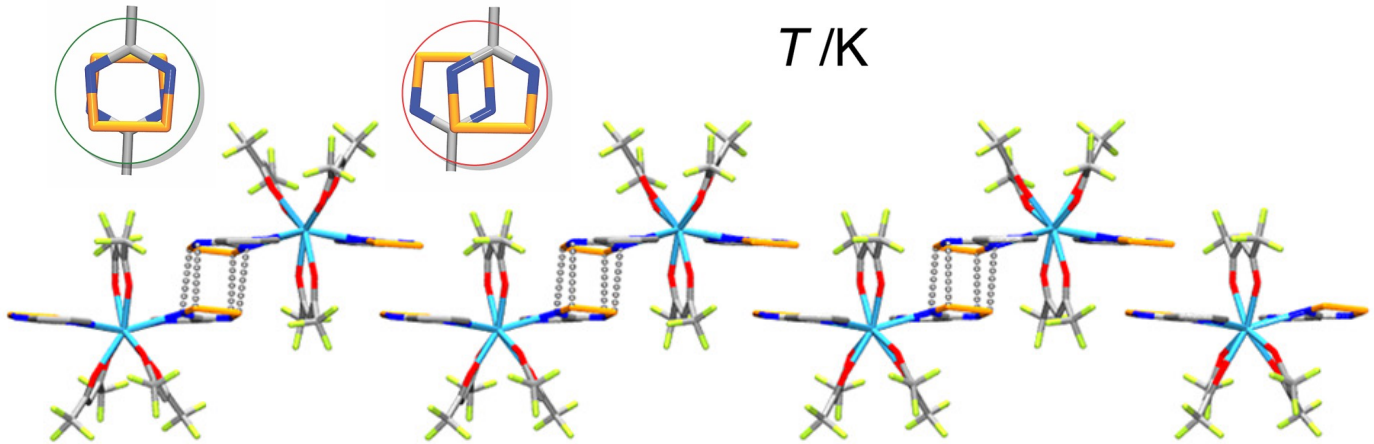
Re-entrant Phase Transition





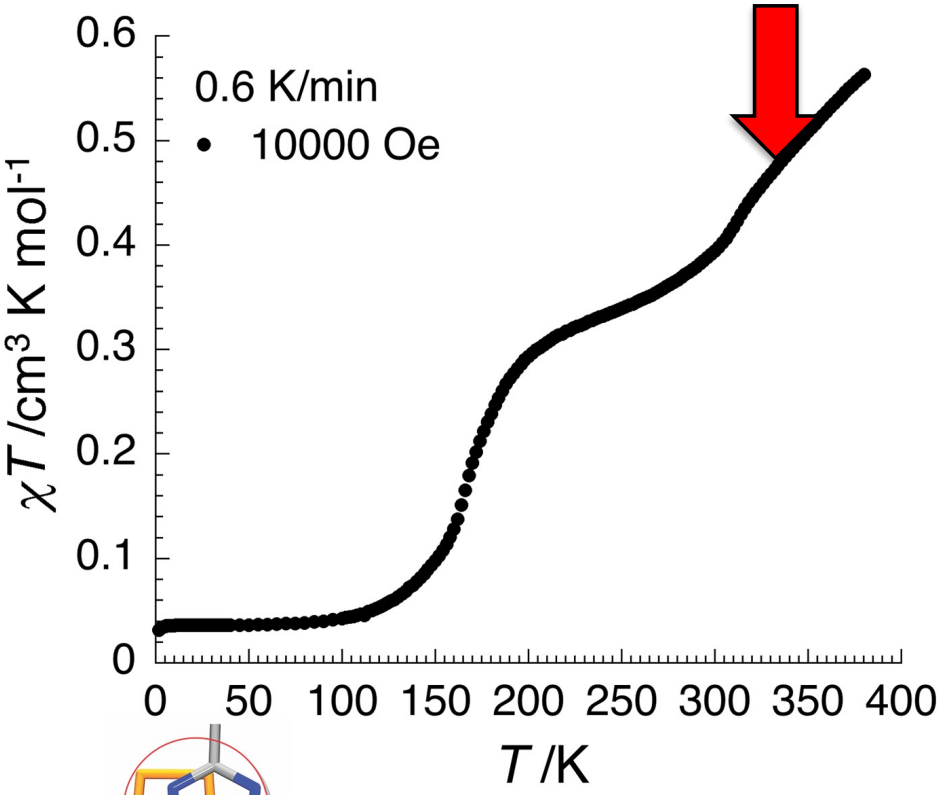


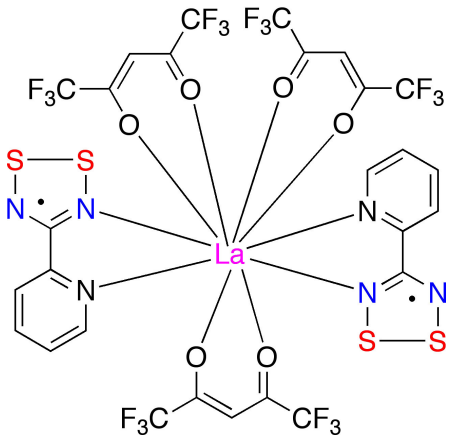
P-1

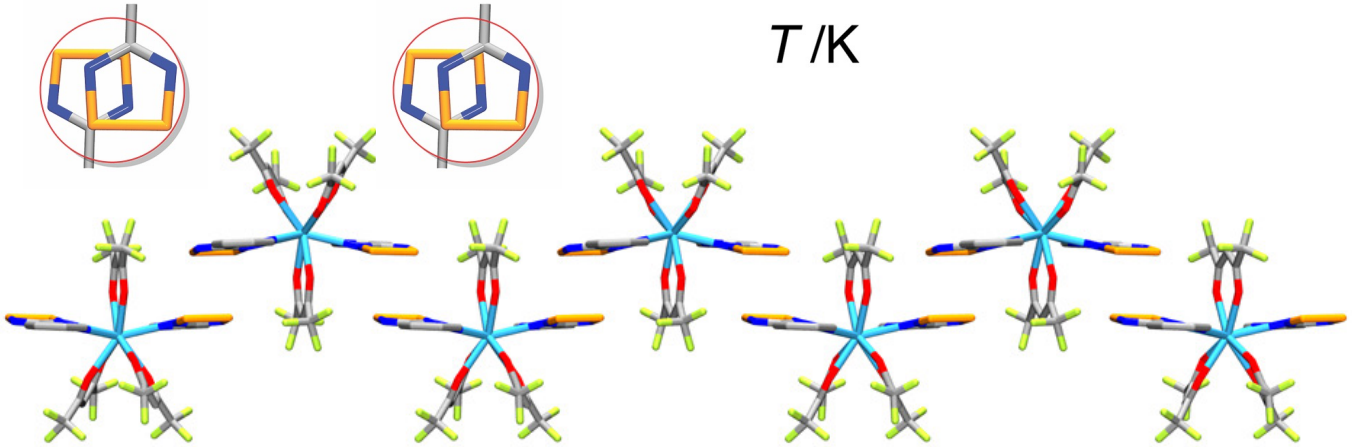
225 K

Preuss, Clérac, Coulon, *et al*. *Chem. Mater*.. **2015**, DOI: 10.1021/acs.chemmater.5b00967.

Re-entrant Phase Transition







*C*2/*c*

340 K

Preuss, Clérac, Coulon, *et al*. *Chem. Mater*.. **2015**, DOI: 10.1021/acs.chemmater.5b00967.

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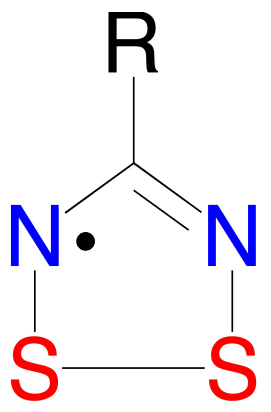
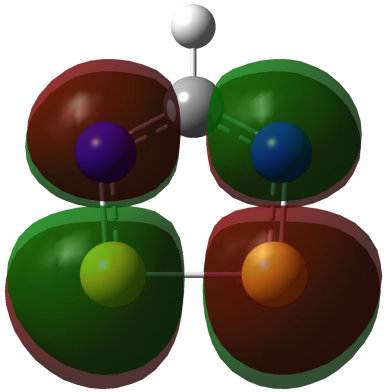
1,2,3,5-DTDA Pancake Bonding

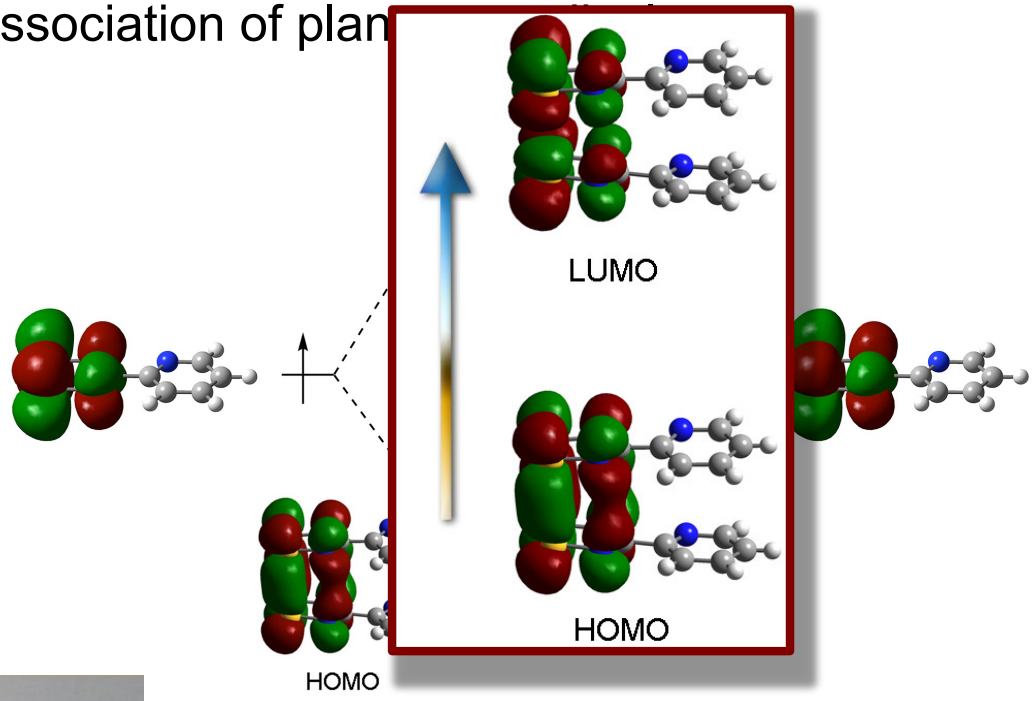
Pair-wise co-facial association of plan

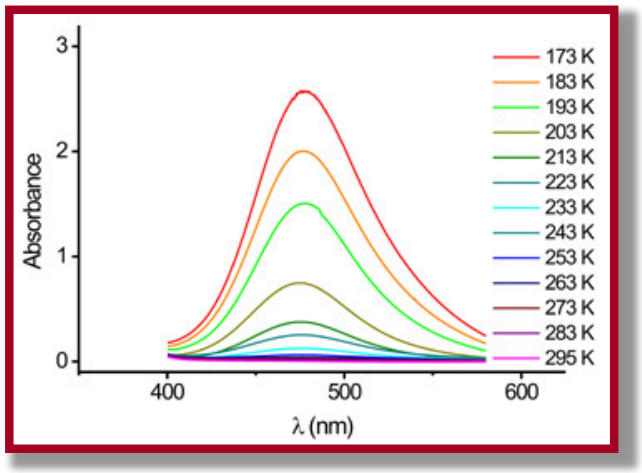


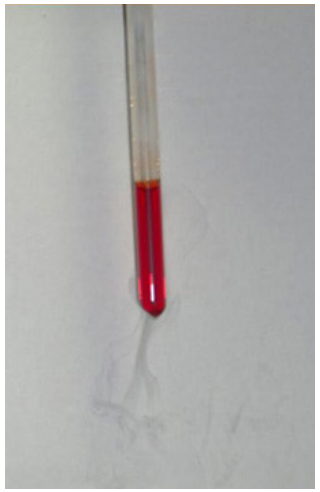
1,2,3,5-Dithiadiazolyl
(DTDA)



SOMO







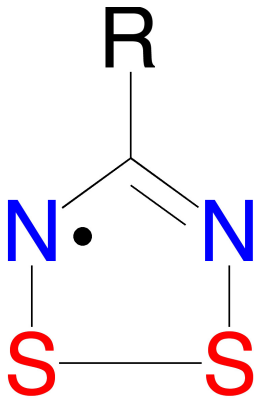
DIAMAGNETIC
DIMERS
In dilute solution
LT

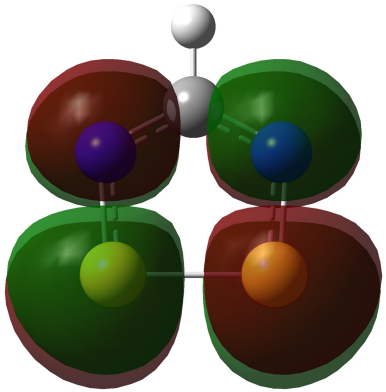
Pancake bonds
reformed

Preuss, *et al., Inorg. Chem.* **2007**, *46*, 3934.

1,2,3,5-DTDA Electrostatics

Sigma-hole type feature & partial charge distribution





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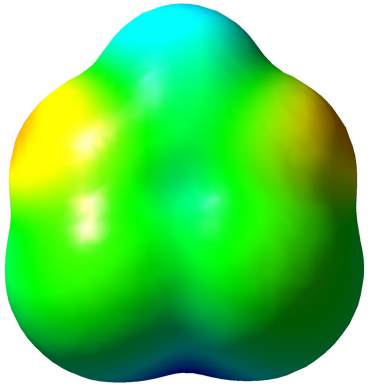
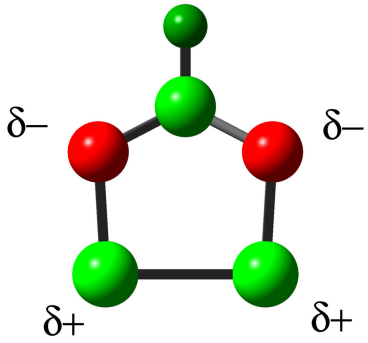


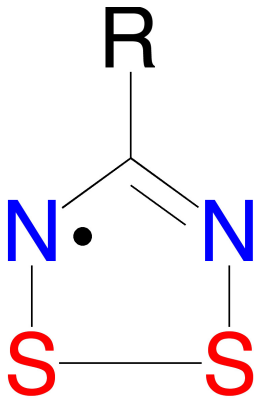
ESP Surface

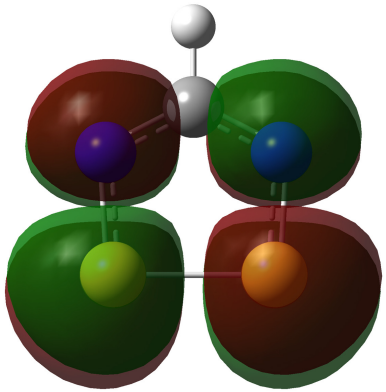


Charge Distribution

1,2,3,5-DTDA Electrostatics

Sigma-hole type feature & partial charge distribution





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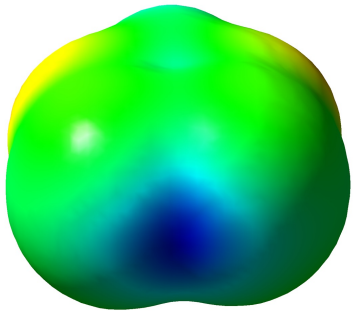
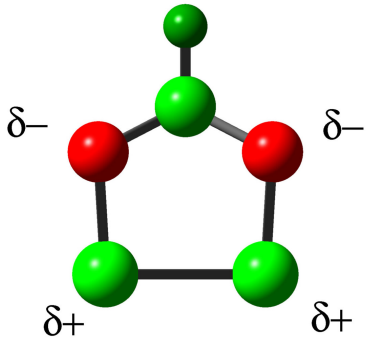


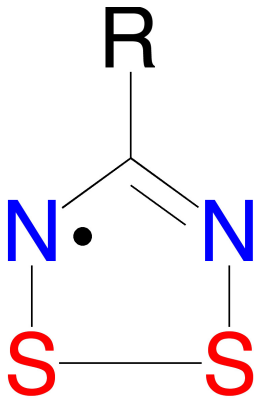
ESP Surface

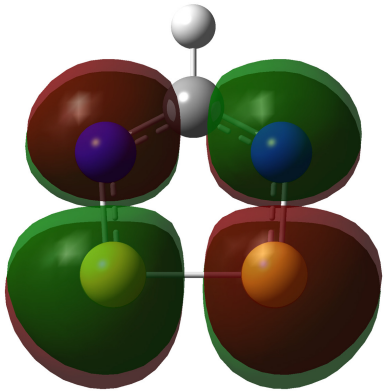


Charge Distribution

1,2,3,5-DTDA Electrostatics

Sigma-hole type feature & partial charge distribution





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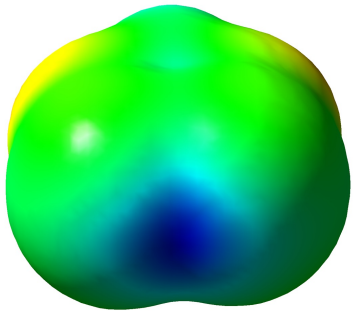
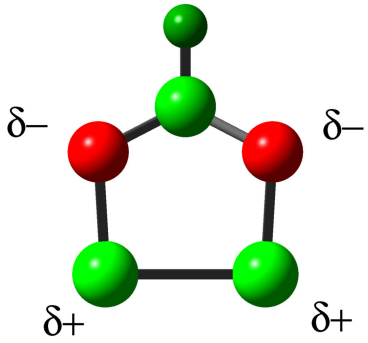
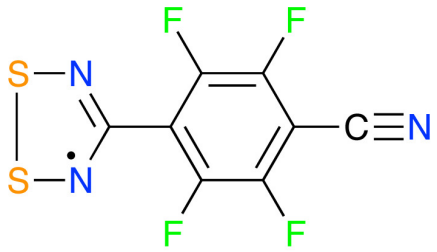


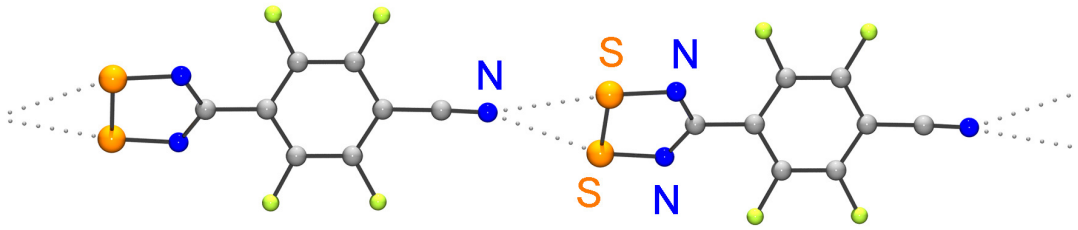
ESP Surface



Charge Distribution



Electrostatic Contacts



Banister, A. J.; Bricklebank, N.; Lavendar, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2533.

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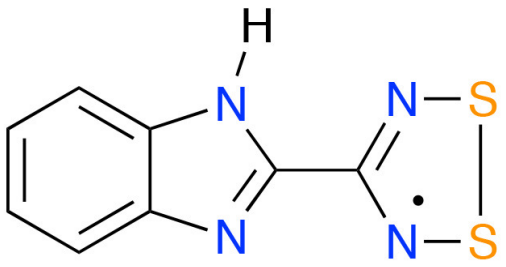
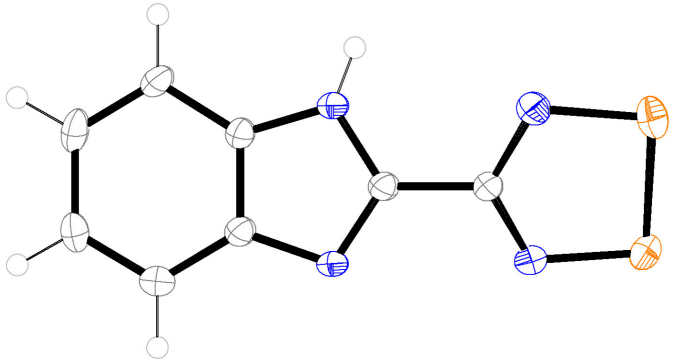
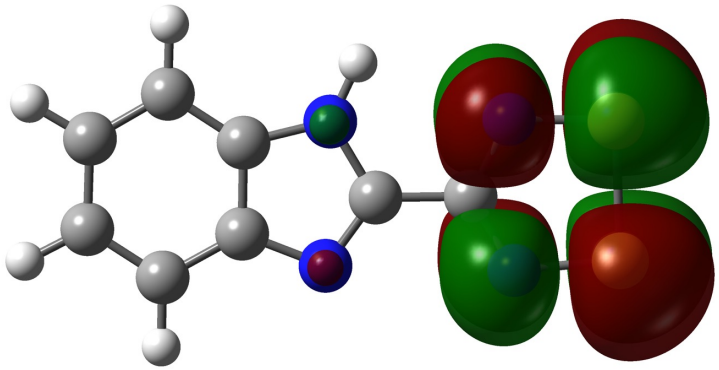
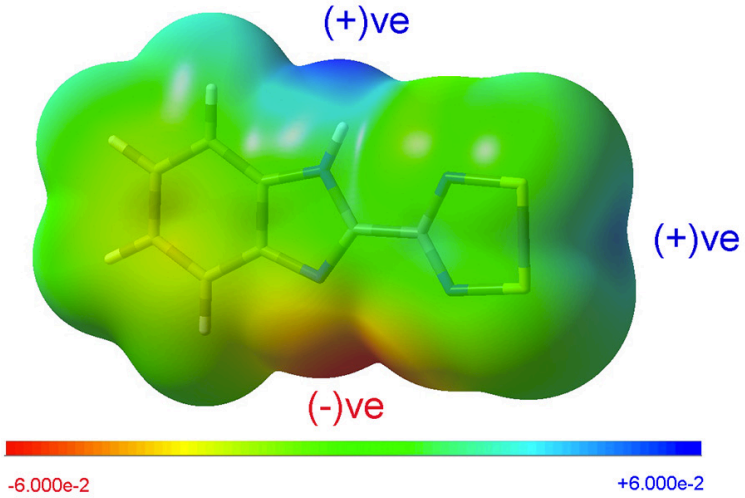
HbimDTDA: MO & ESP

HbimDTDA









Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

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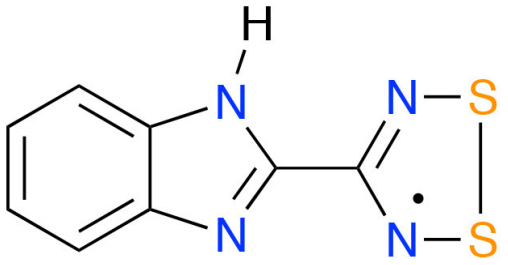
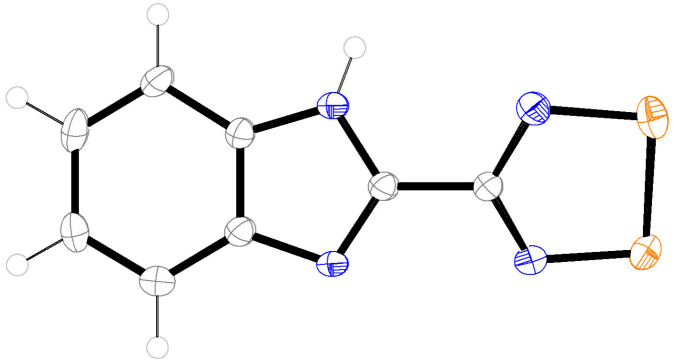
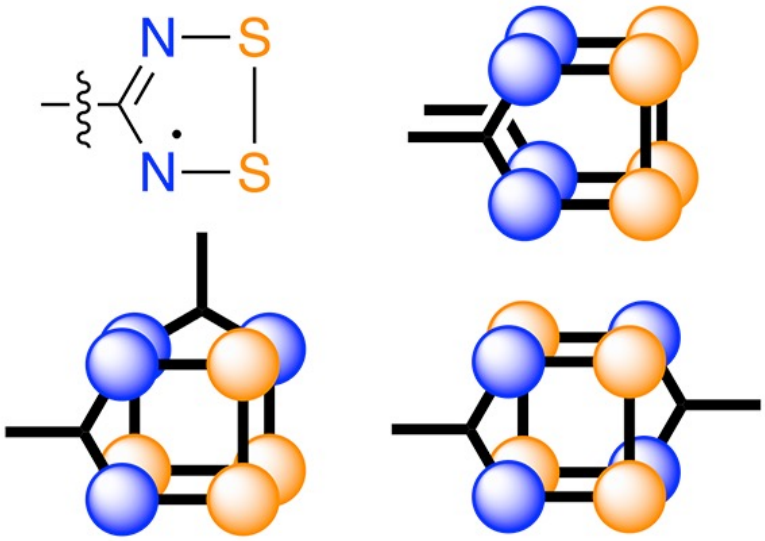
HbimDTDA: Pancake vs. H-bond

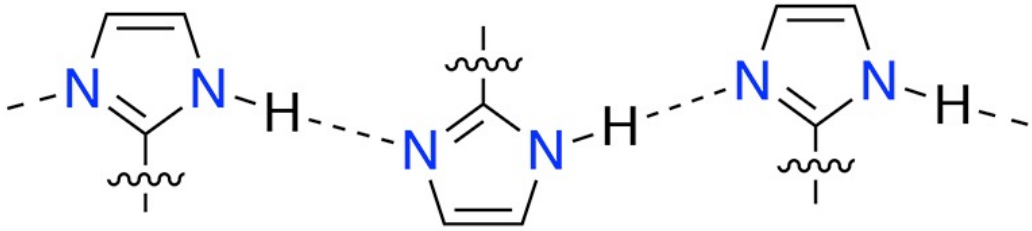
HbimDTDA







pancake bonded

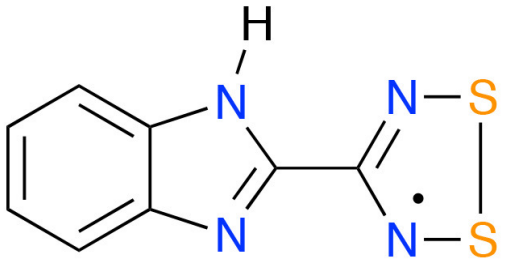


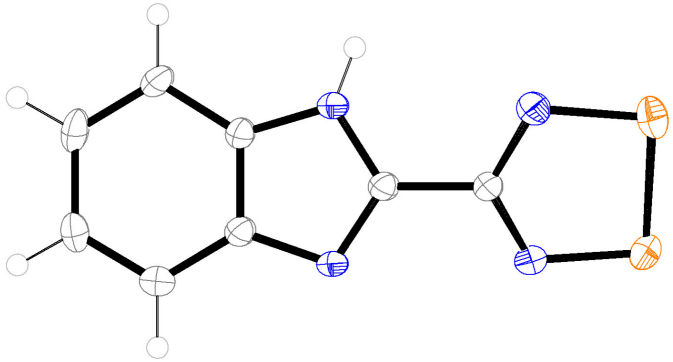
H-bonded imidazole chain structure

Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

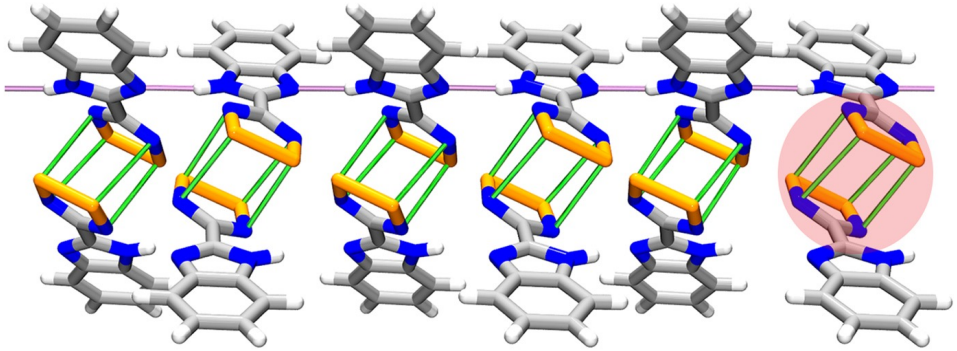
HbimDTDA: 100 K structure

HbimDTDA





100 K



Pancake bonds
&
H-bonds

Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

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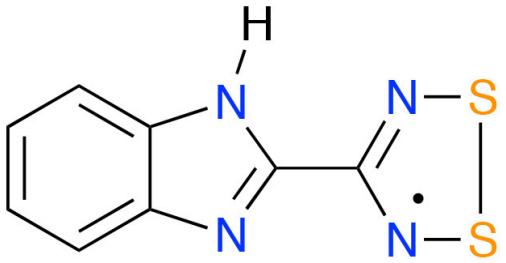
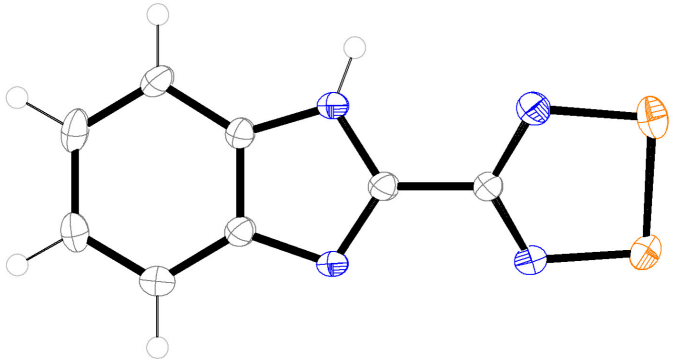
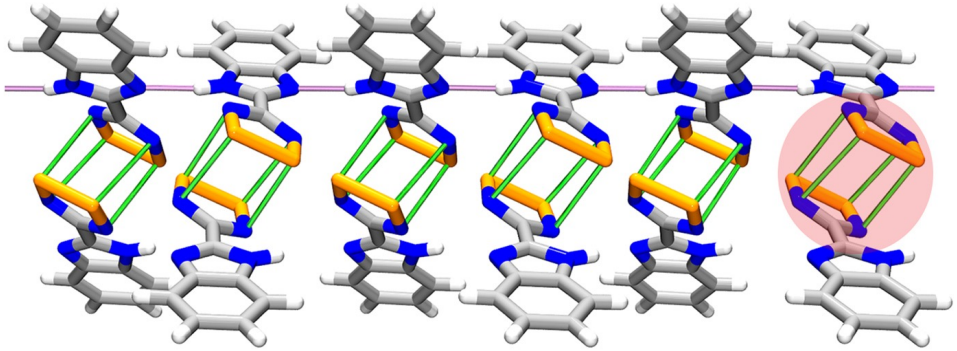
HbimDTDA: 340 K structure

HbimDTDA



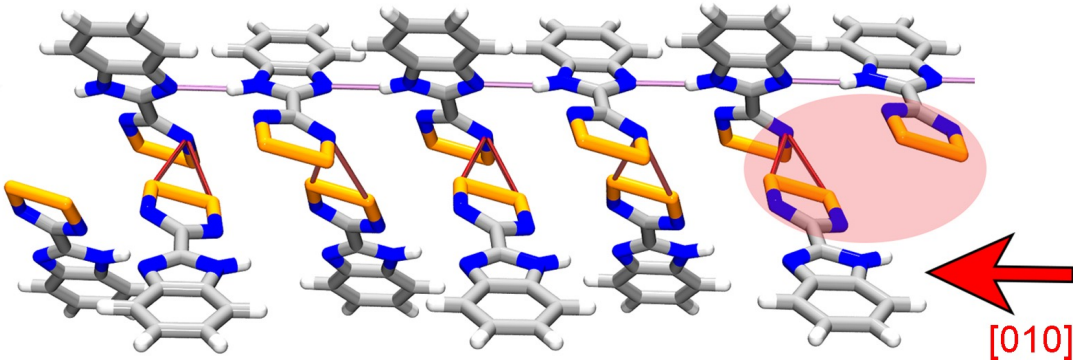


100 K



Pancake bonds
&
H-bonds

340 K



~~Pancake bonds~~
&
H-bonds

Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

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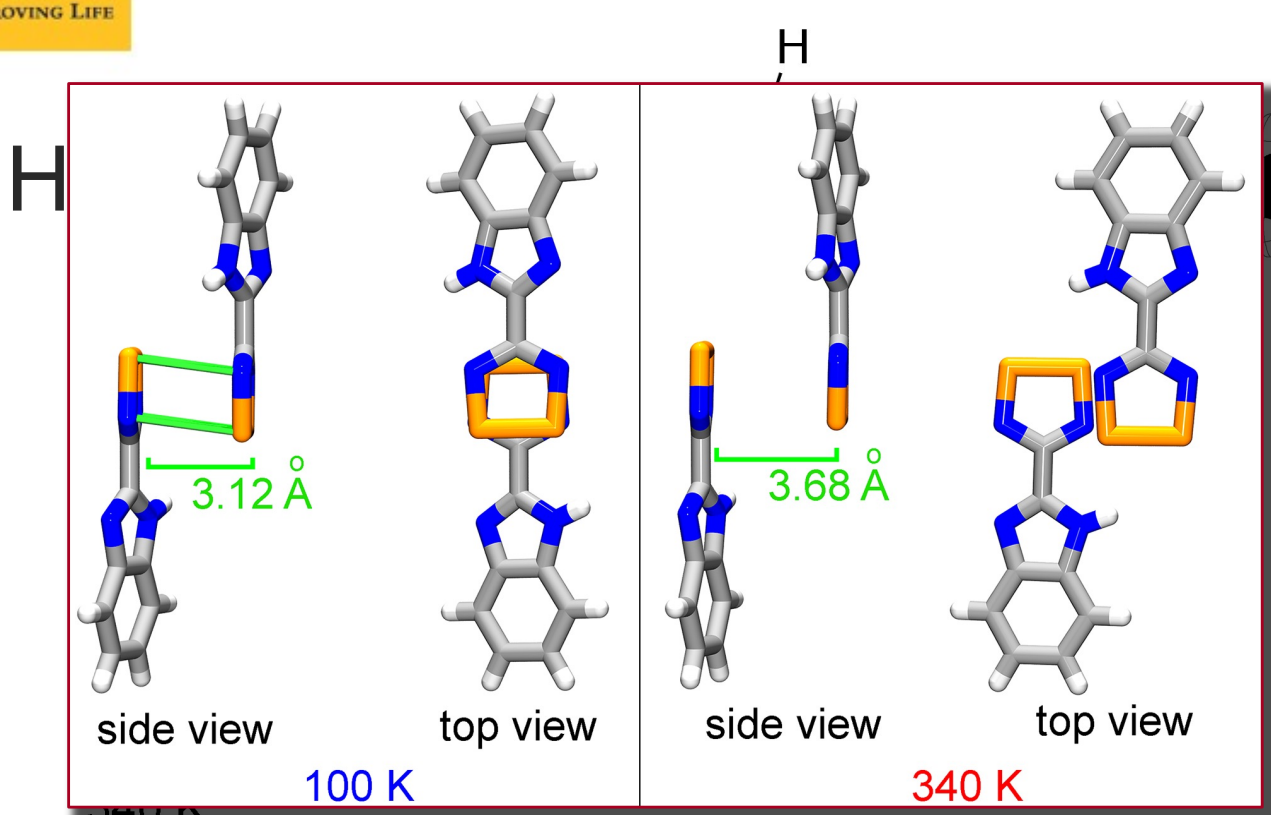
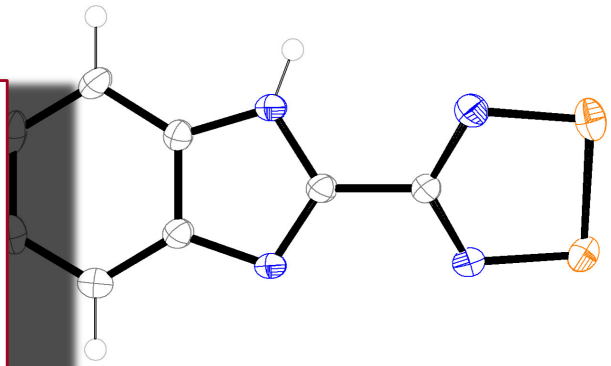
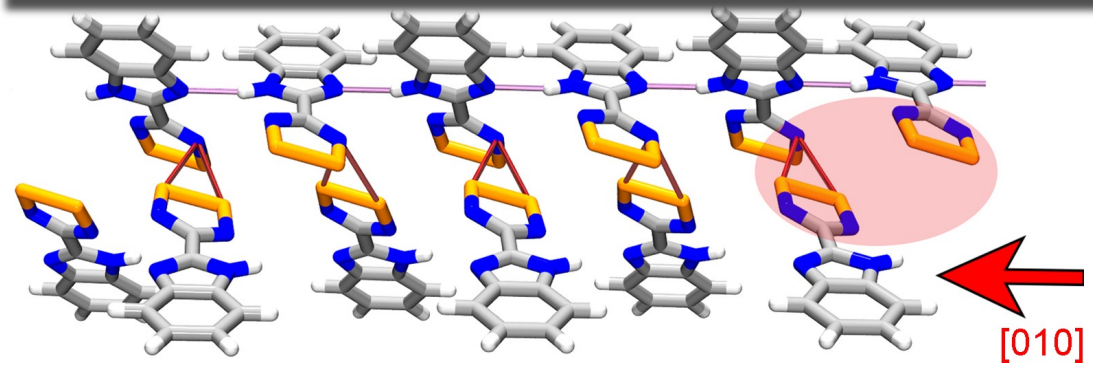
HbimDTDA: Pancake Bonding





Pancake bonds
&
H-bonds



~~Pancake bonds~~
&
H-bonds

Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

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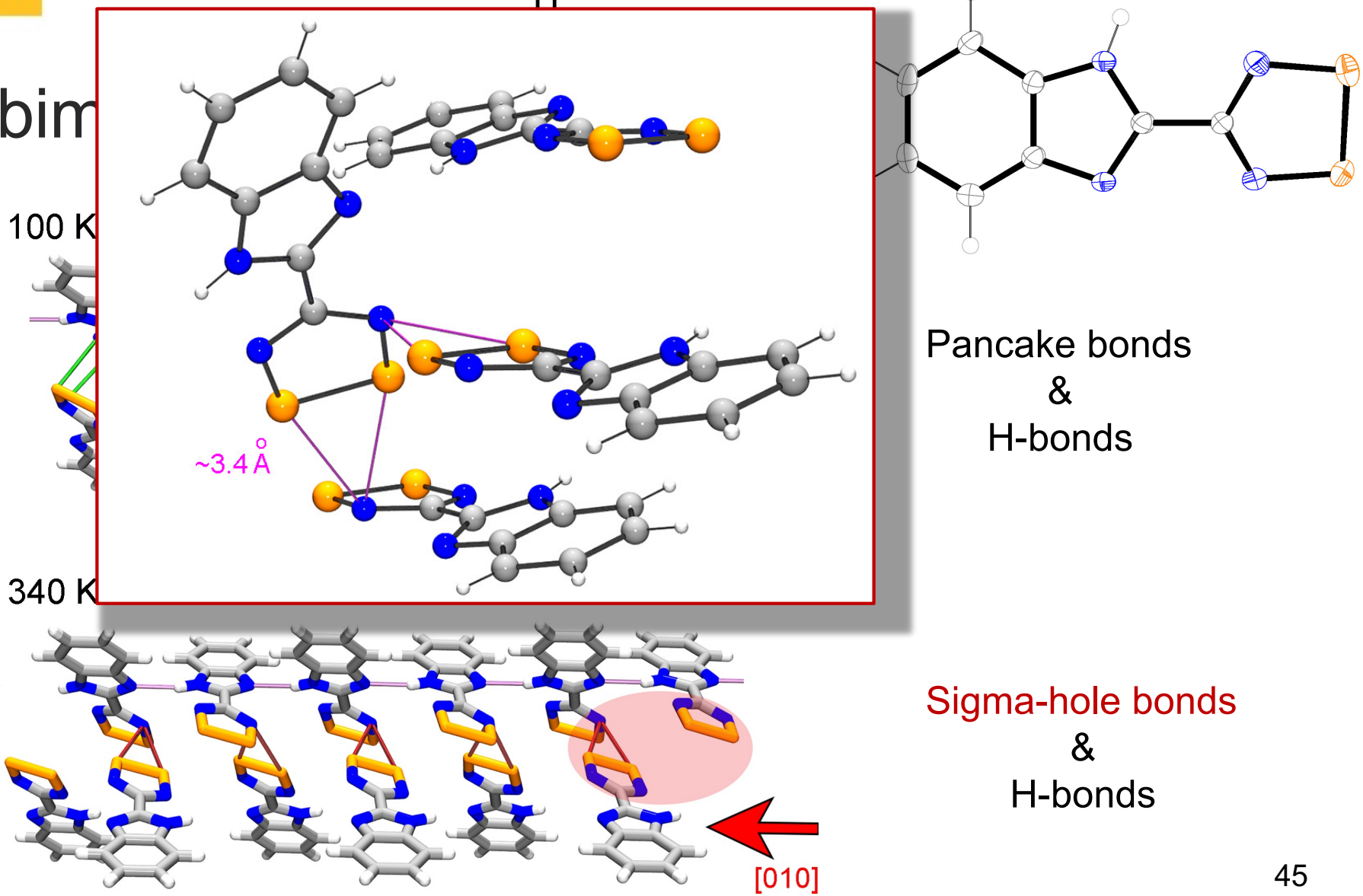
HbimDTDA: Sigma-hole bonding

Hbim



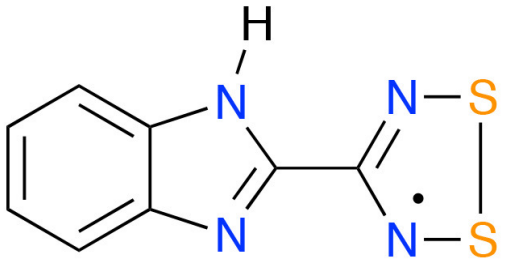
Pancake bonds
&
H-bonds

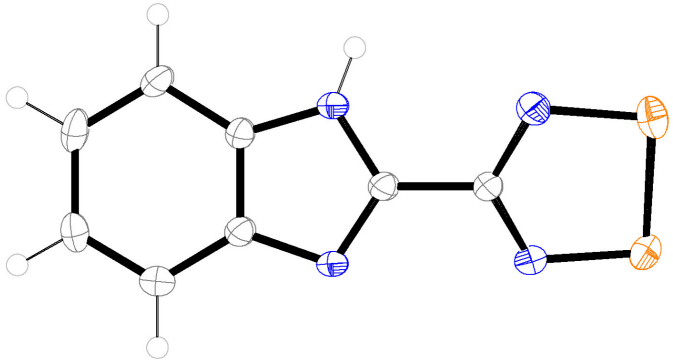
Sigma-hole bonds
&
H-bonds

Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

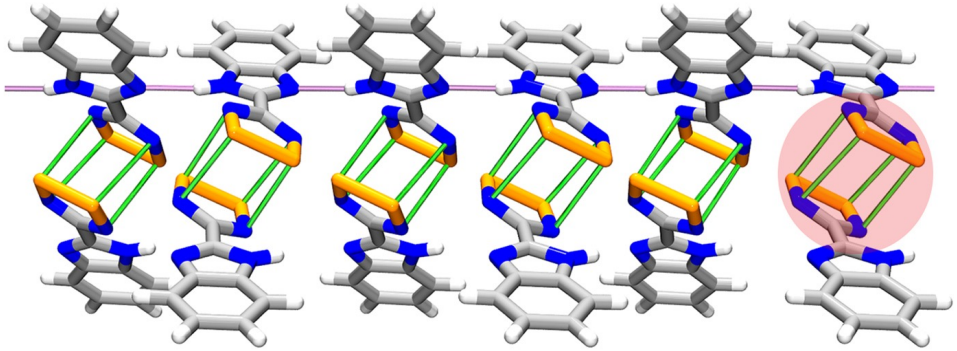
HbimDTDA: PXRD

HbimDTDA

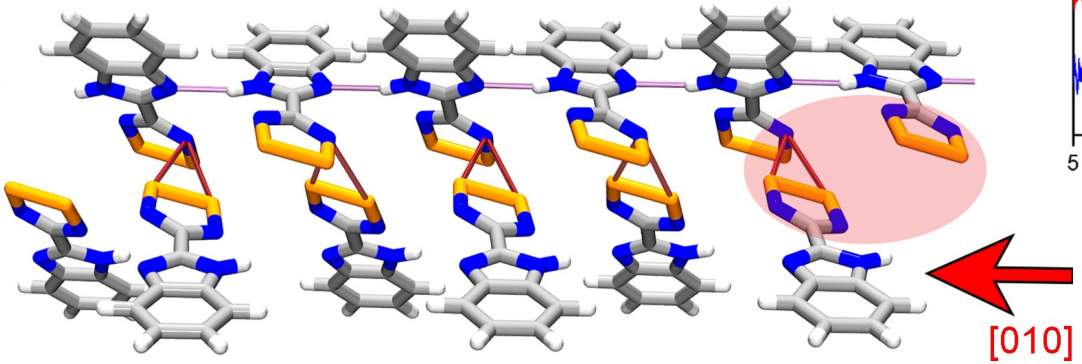


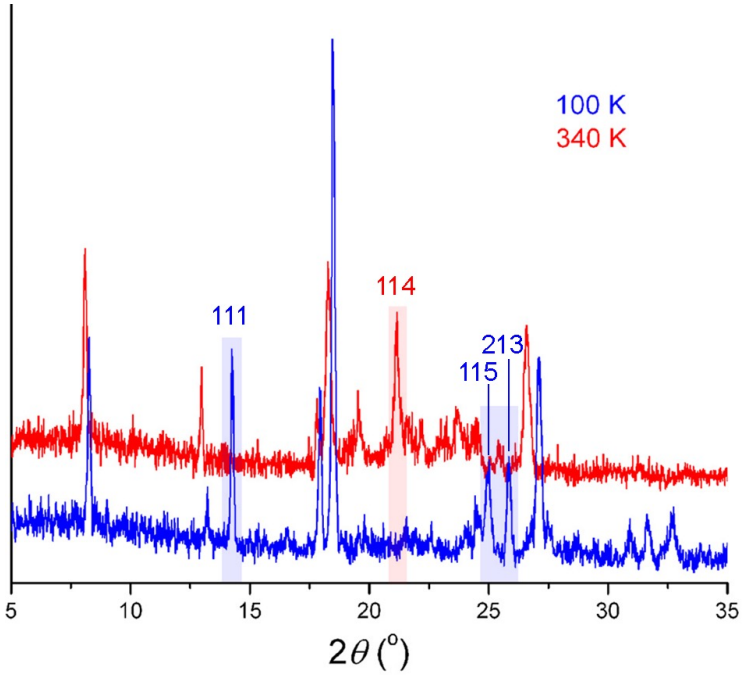


100 K



340 K





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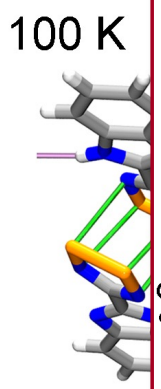
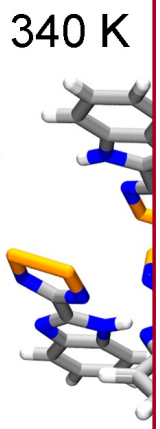
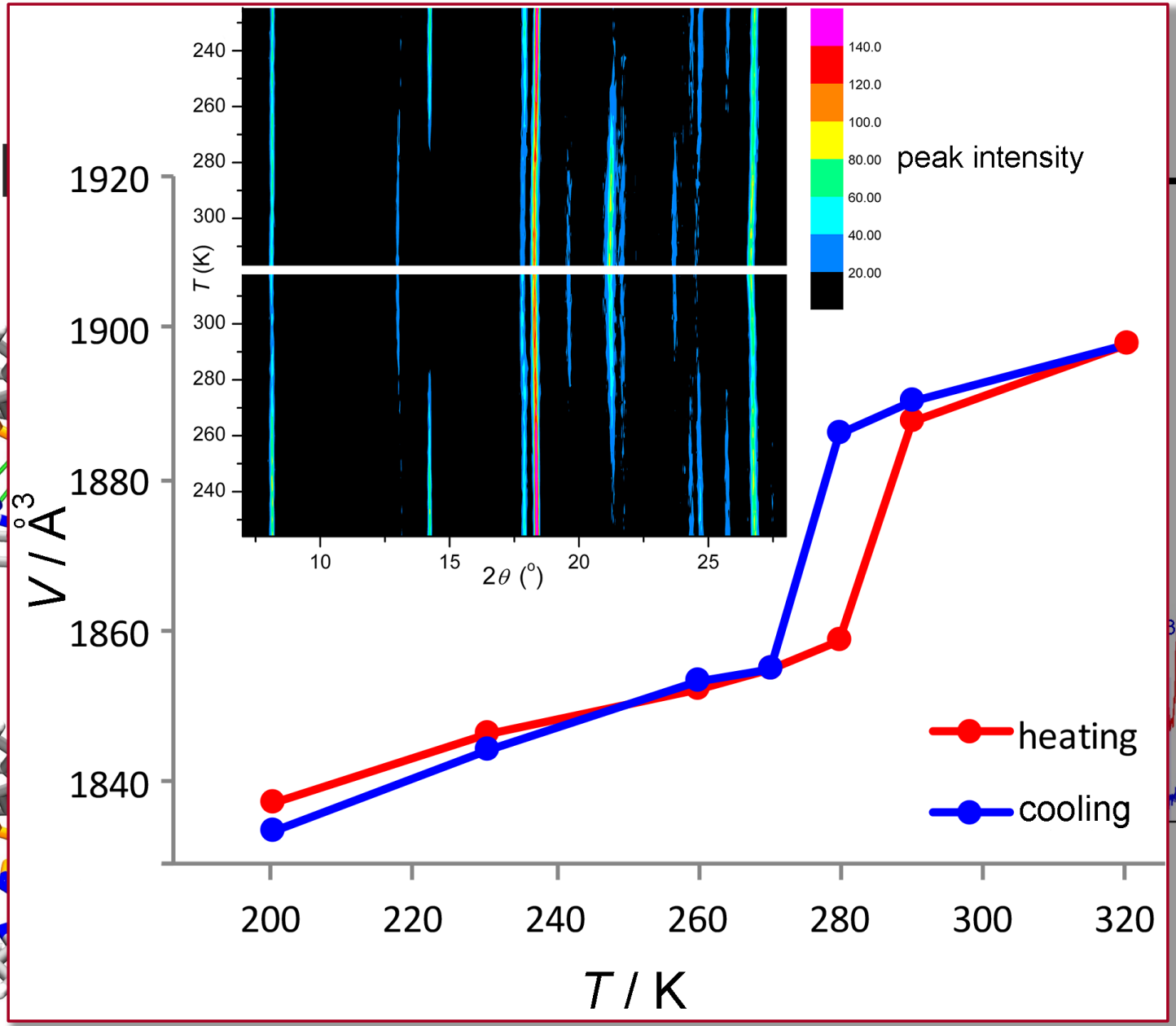
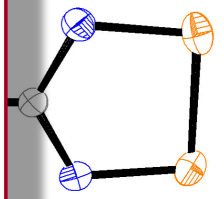
HbimDTDA: PXRD …hysteresis!

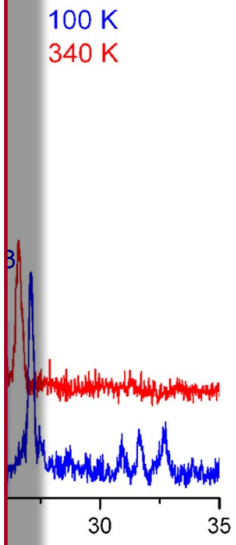
Hbiml











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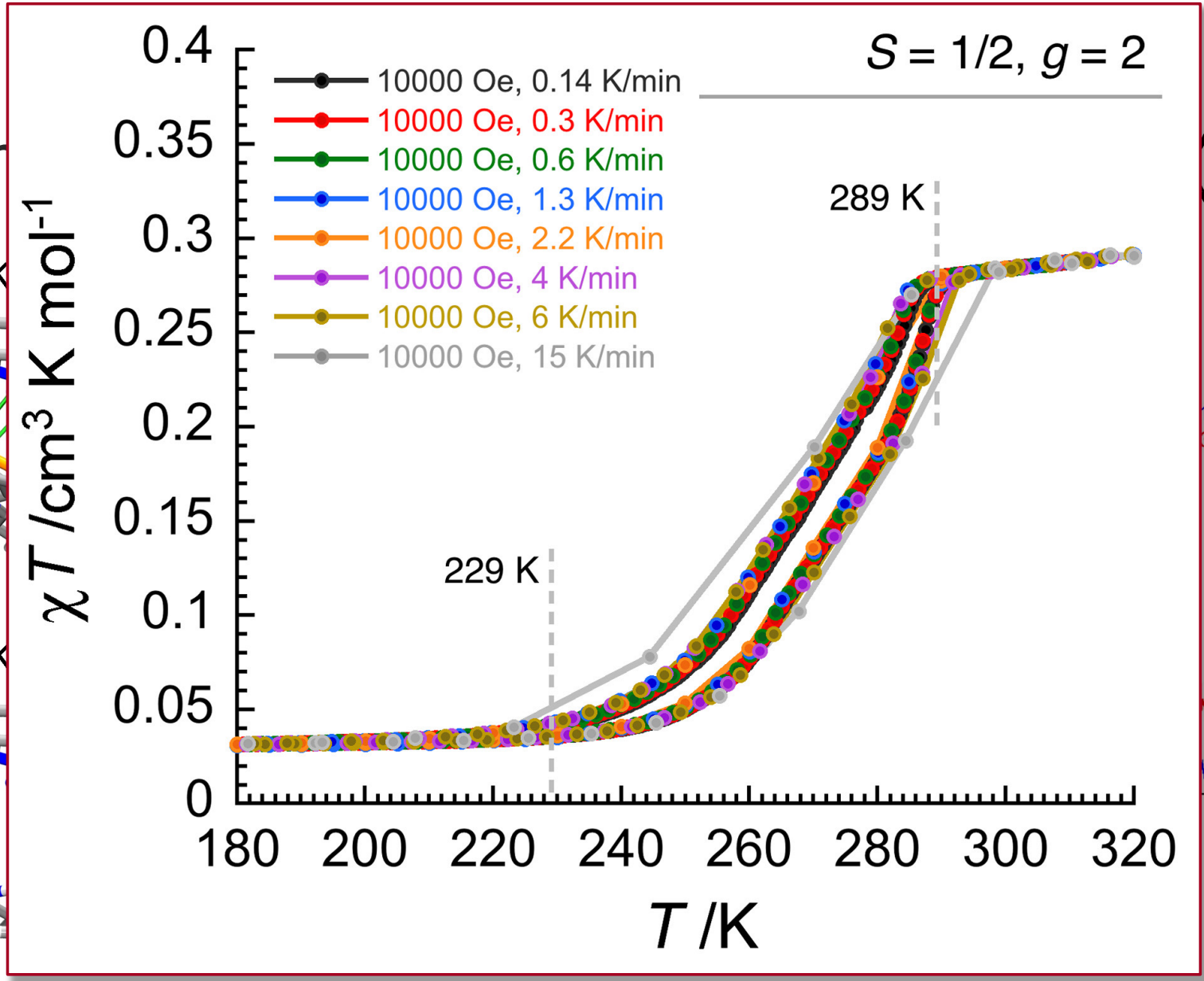
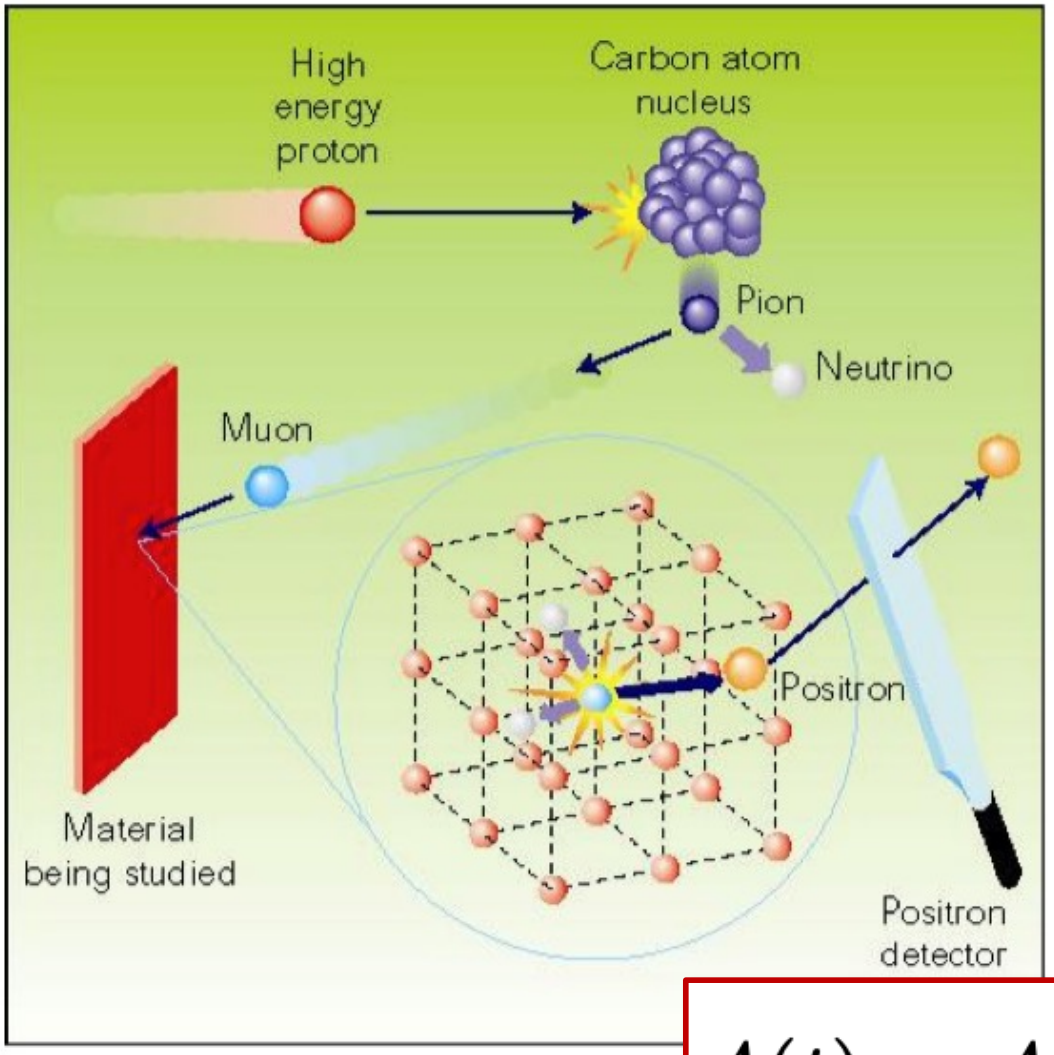
HbimDTDA: Magnetic hysteresis

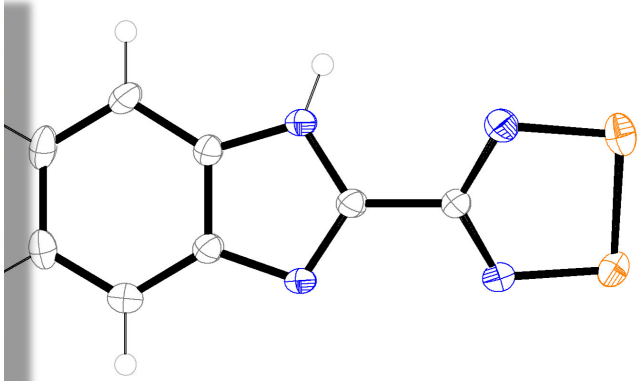


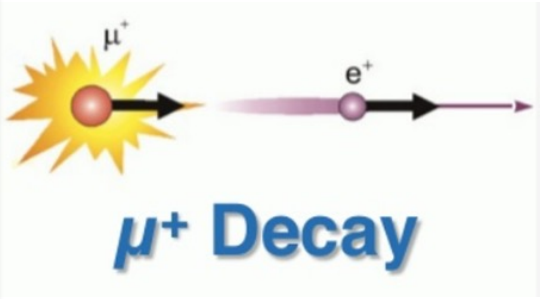
Mills, M. B.; Wohlhauser, T.; Stein, B.; Verduyn, W. R.; Song, E.; Dechambenoit, P.; Rouzières, M.; Clérac, R.; Preuss, K. E. *J. Am. Chem. Soc.* **2018**, *140*, 16904.

HbimDTDA: μ^+SR

Hbir

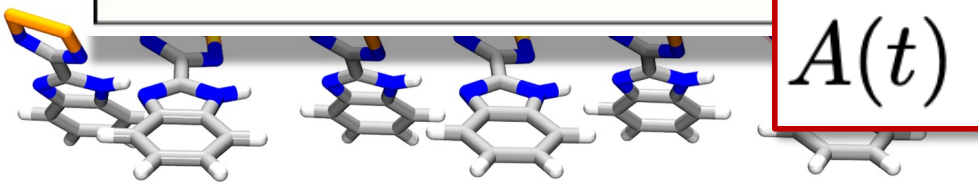






100

340



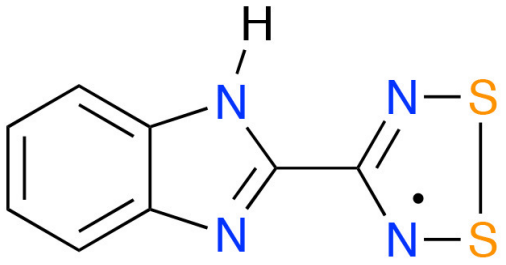
[010]

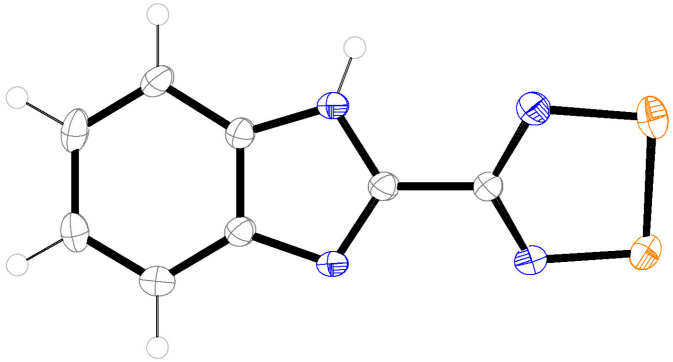
$$A(t) = A_{\mathrm{r}} e^{-(\lambda t)^{\beta}} + A_{\mathrm{b}}$$

Hernandez-Melian, A.; Huddart, B. M.; Pratt, F. L.; Blundell, S. J.; Mills, M.; Young, H. K. S.; Preuss, K. E.; Lancaster, T. *J. Phys. Chem. Solids*, **2023**, *181*, 111493.

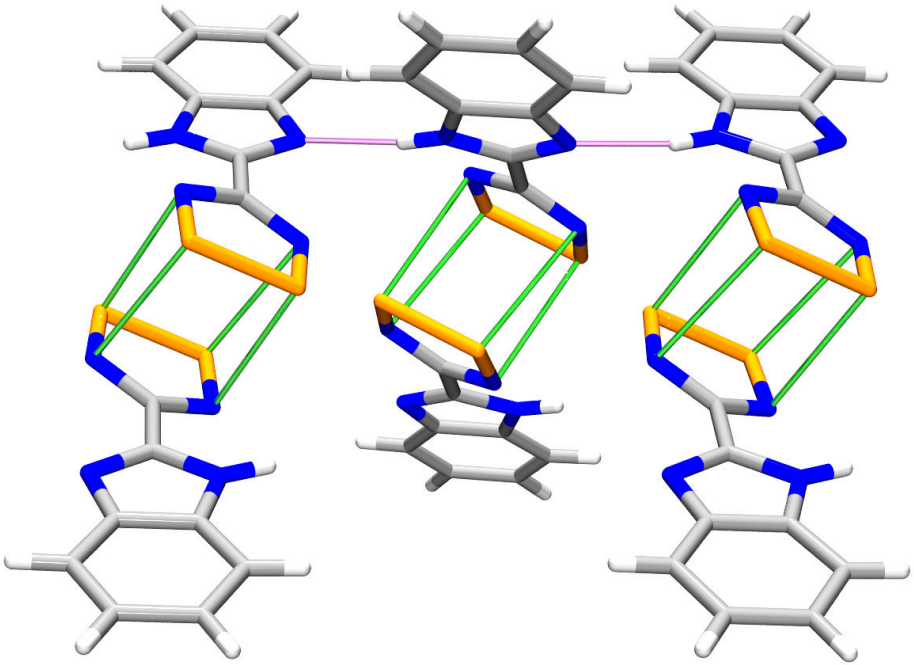
HbimDTDA: μ^+SR

HbimDTDA





100 K



Where are the muons?

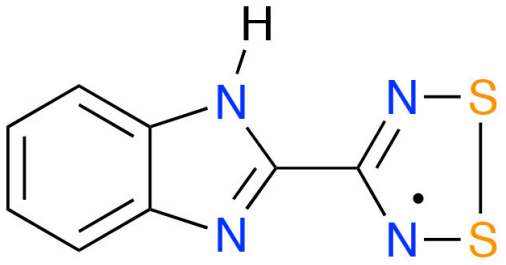
DFT using artificially-lightened H atom

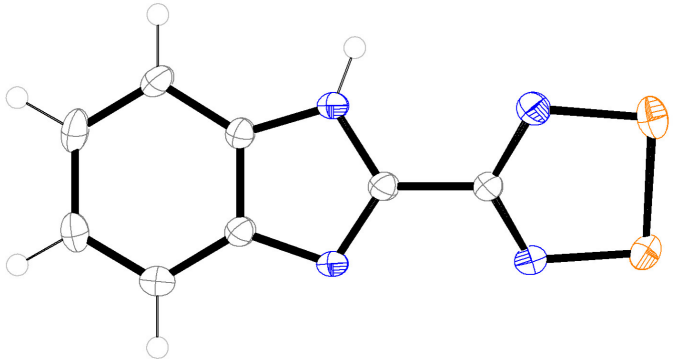
→ +mu

Hernandez-Melian, A.; Huddart, B. M.; Pratt, F. L.; Blundell, S. J.; Mills, M.; Young, H. K. S.; Preuss, K. E.; Lancaster, T. *J. Phys. Chem. Solids*, **2023**, *181*, 111493.

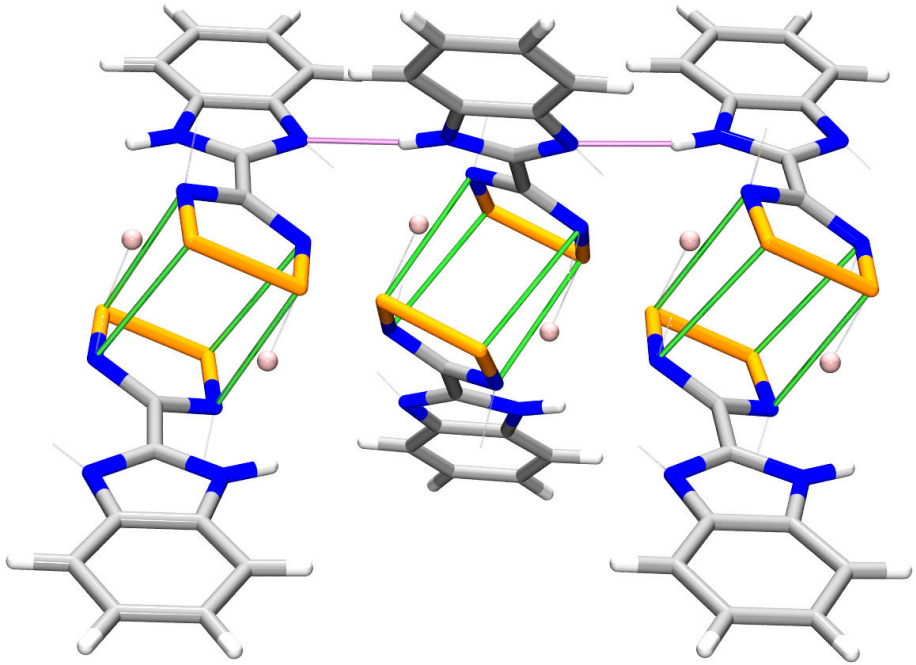
HbimDTDA: μ^+SR

HbimDTDA





100 K



Where are the muons?

DFT using artificially-lightened H atom
→ +mu

site 1

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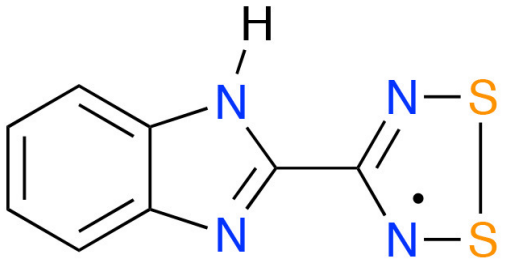
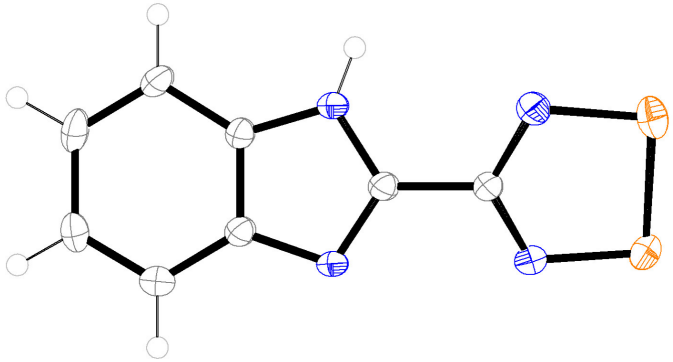
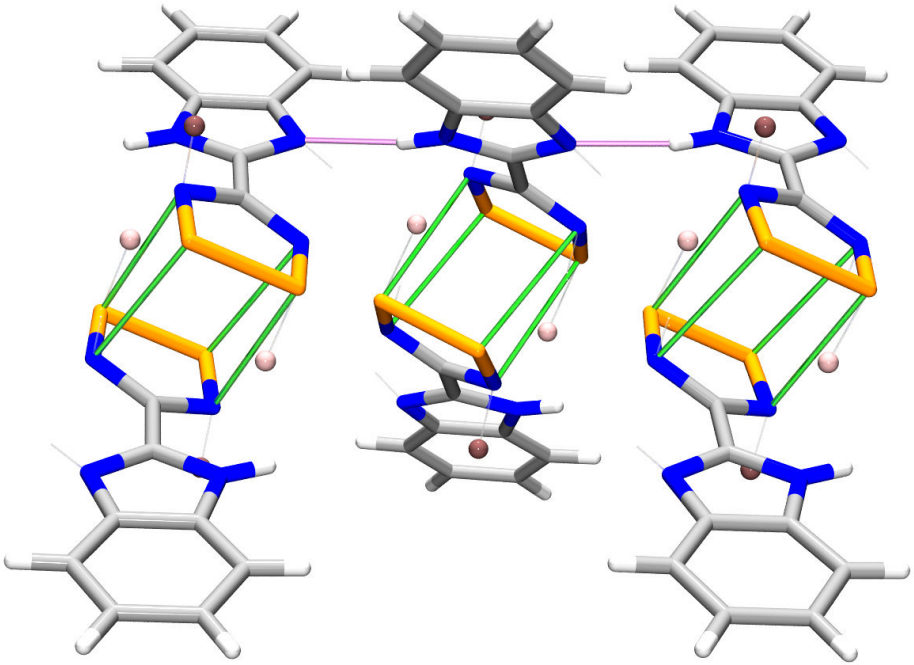
HbimDTDA: μ^+SR

HbimDTDA





100 K



Where are the muons?

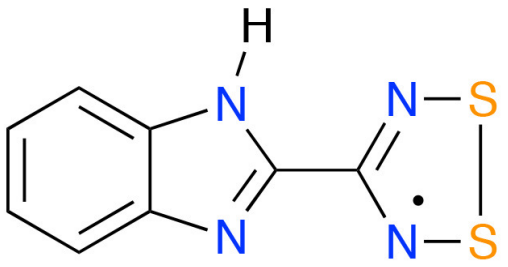
DFT using artificially-lightened H atom
→ +mu

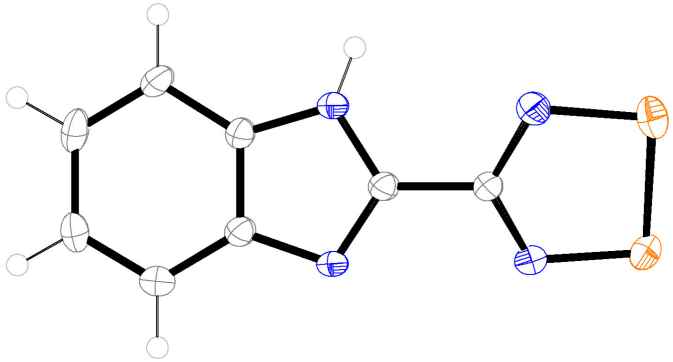
site 1
site 2

Hernandez-Melian, A.; Huddart, B. M.; Pratt, F. L.; Blundell, S. J.; Mills, M.; Young, H. K. S.; Preuss, K. E.; Lancaster, T. *J. Phys. Chem. Solids*, **2023**, *181*, 111493.

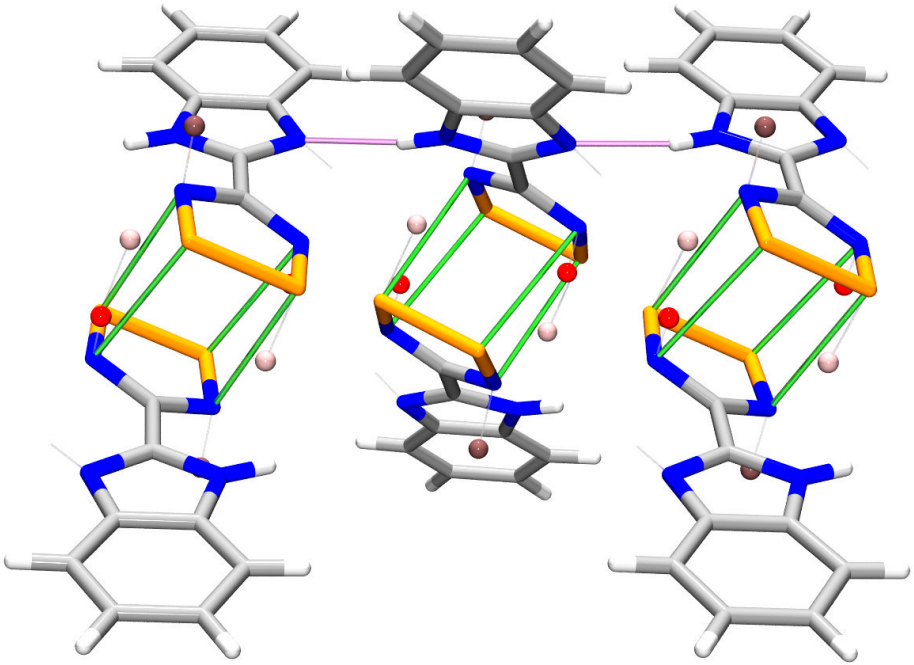
HbimDTDA: μ^+SR

HbimDTDA





100 K



Where are the muons?

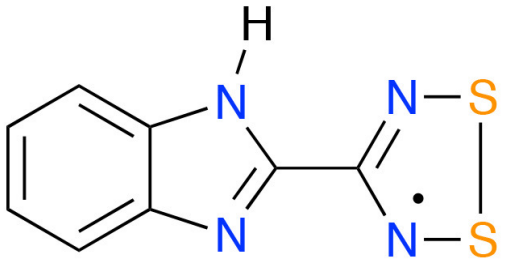
DFT using artificially-lightened H atom
→ +mu

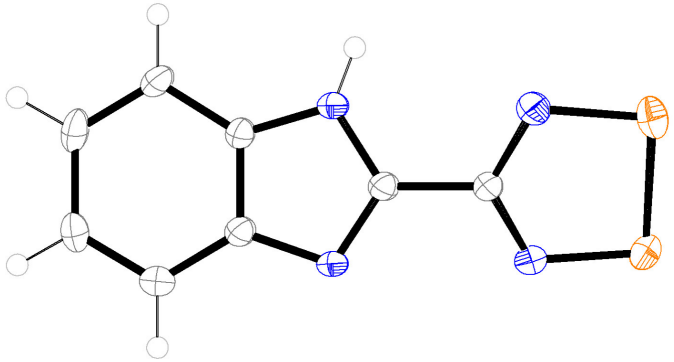
site 1
site 2
site 3

Hernandez-Melian, A.; Huddart, B. M.; Pratt, F. L.; Blundell, S. J.; Mills, M.; Young, H. K. S.; Preuss, K. E.; Lancaster, T. *J. Phys. Chem. Solids*, **2023**, *181*, 111493.

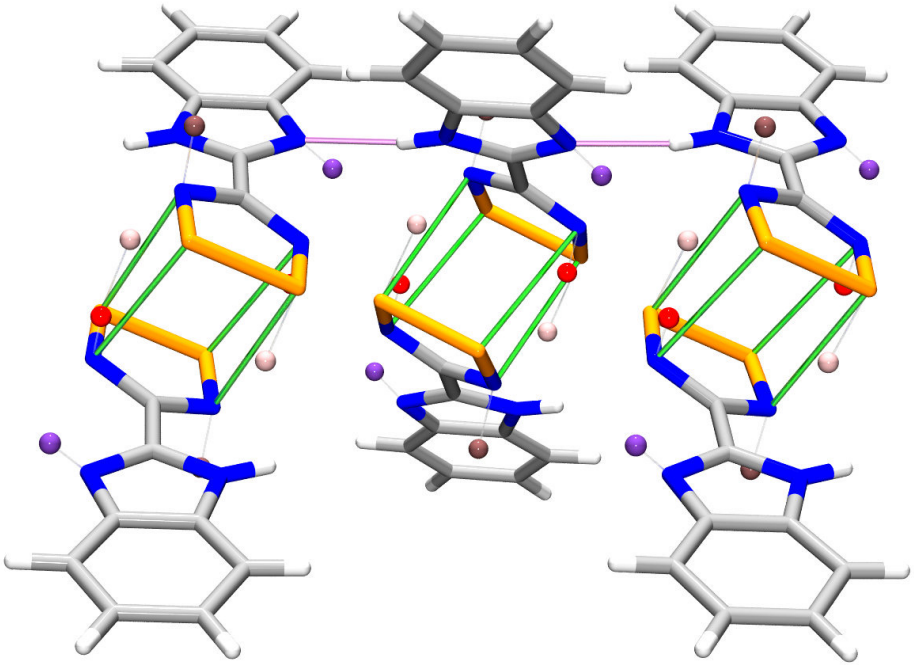
HbimDTDA: μ^+SR

HbimDTDA





100 K



Where are the muons?

DFT using artificially-lightened H atom
→ +mu

site 1
site 2
site 3
site 4

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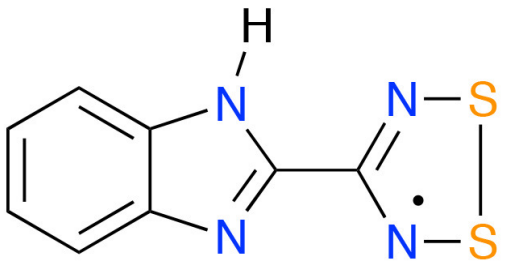
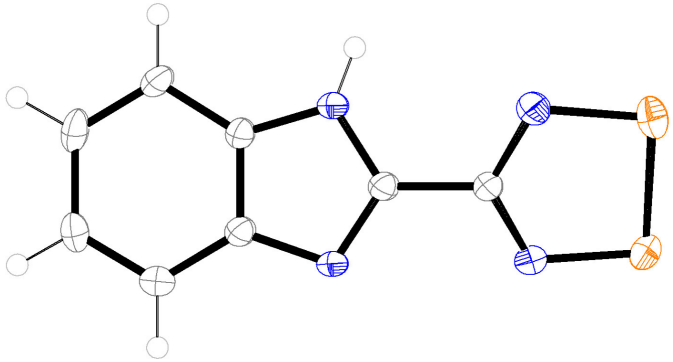
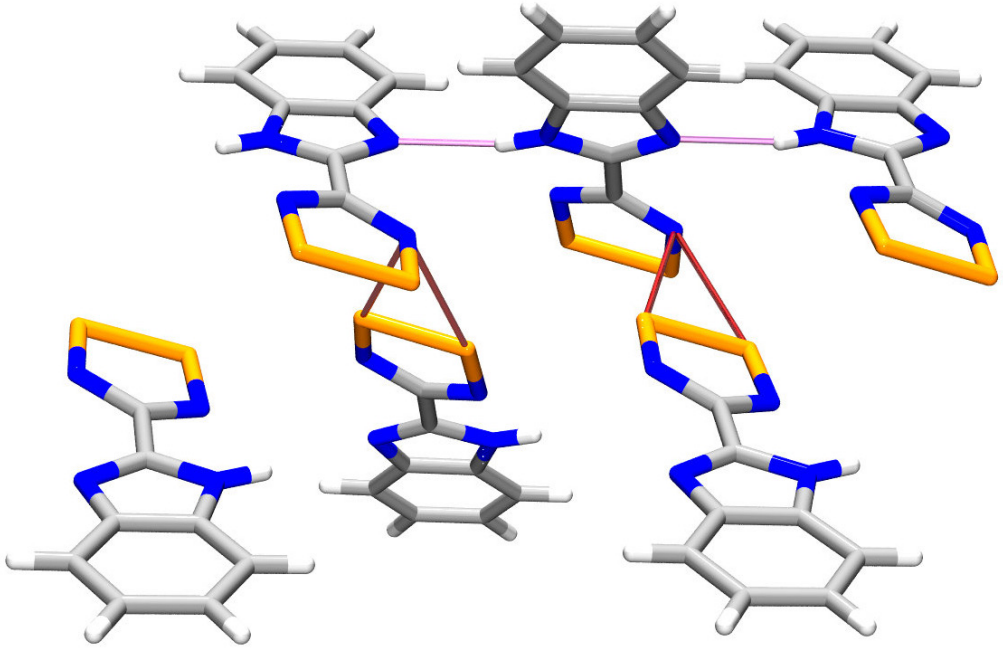




340 K



Where are the muons?

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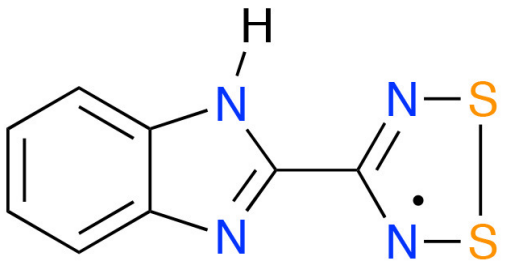

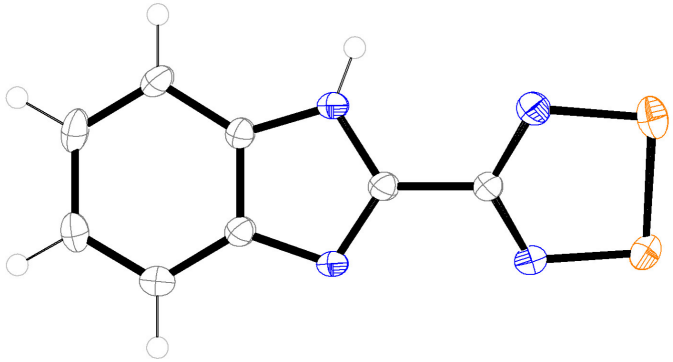

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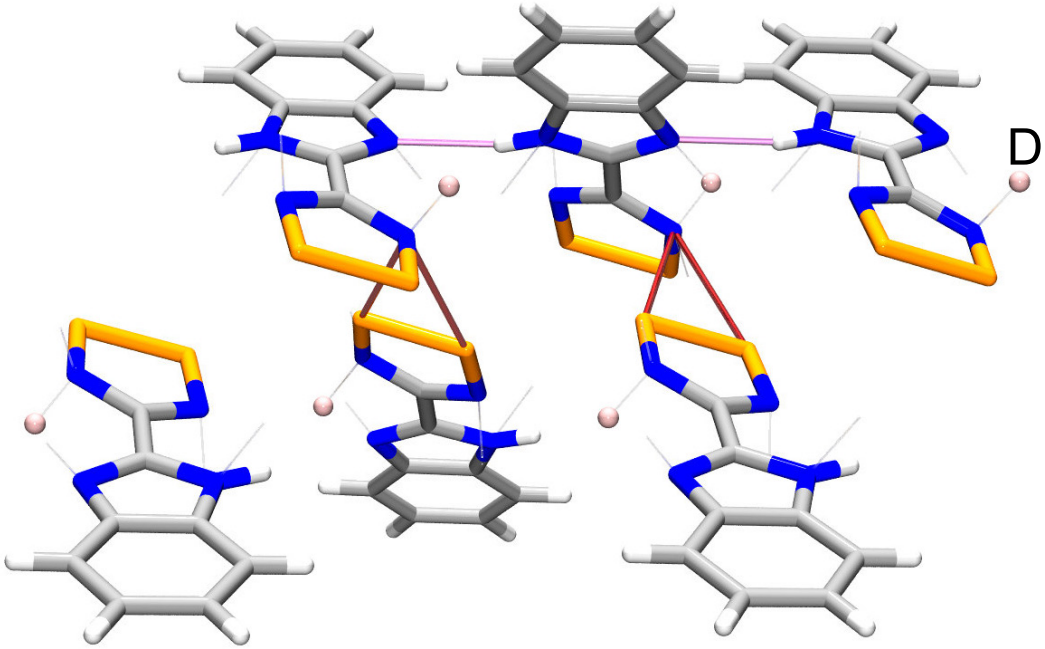

Where are the muons?

DFT using artificially-lightened H atom

→ +mu

site 1

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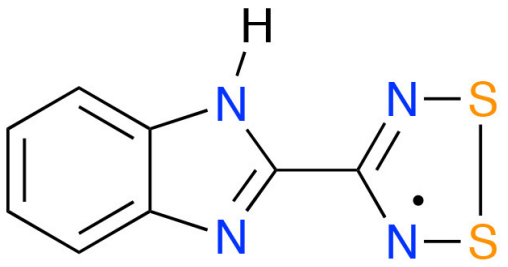

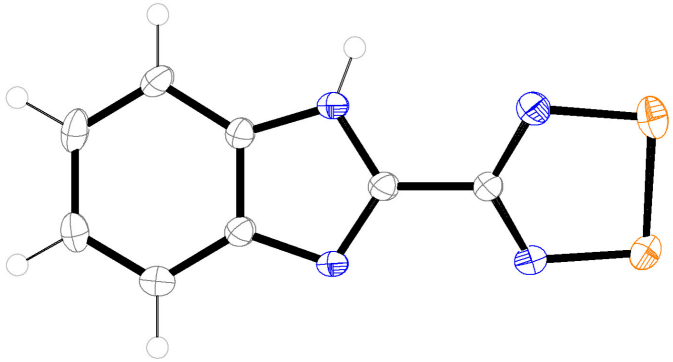

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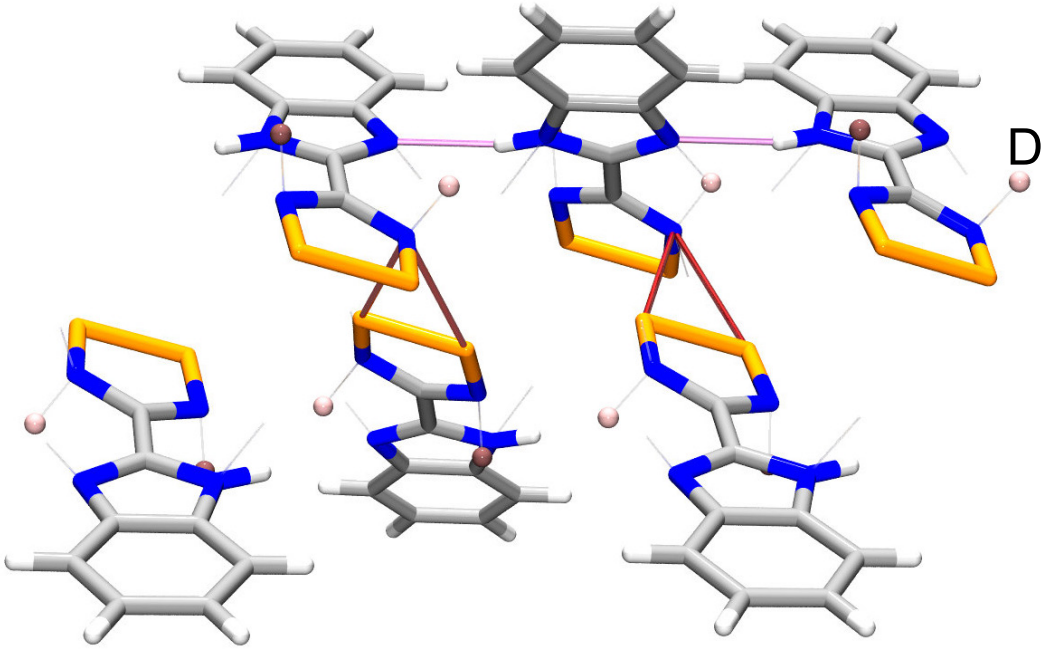

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site 2

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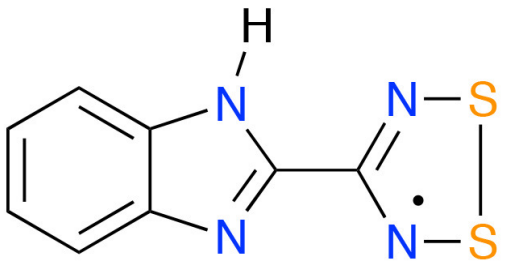

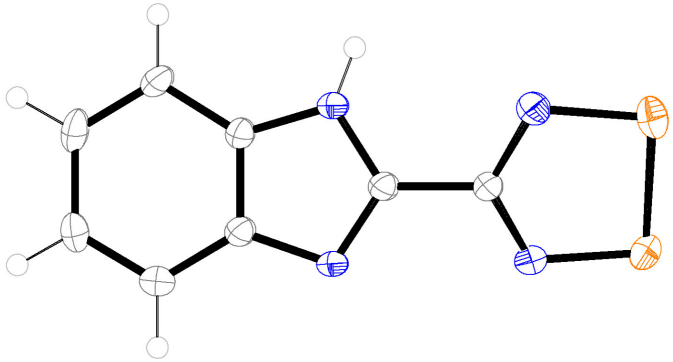

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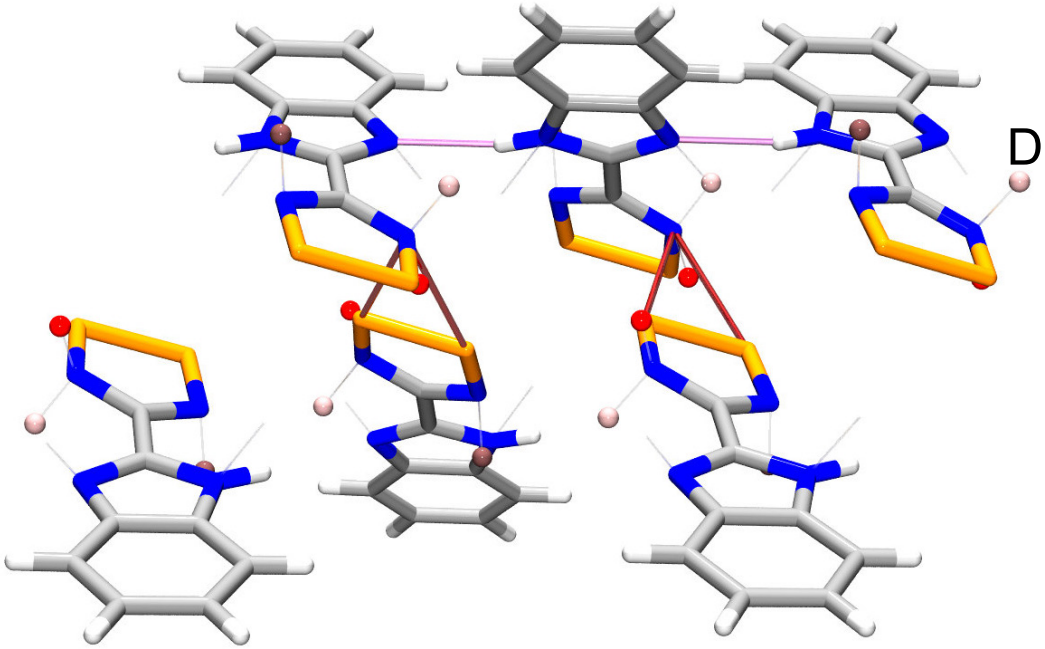

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site 3

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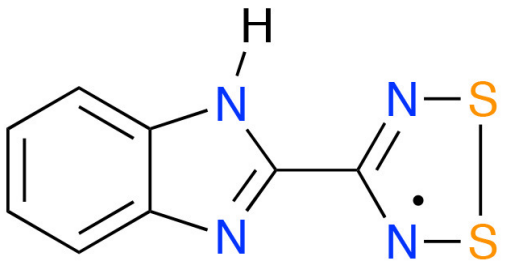

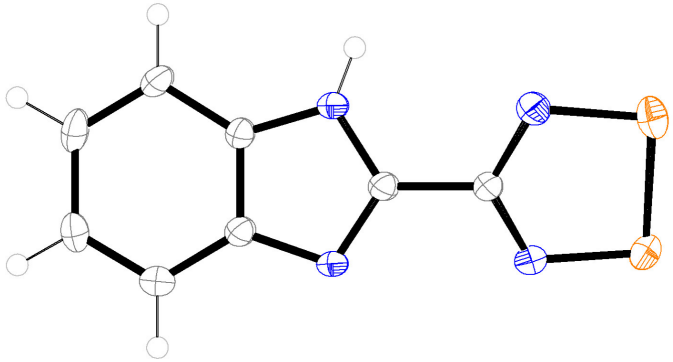

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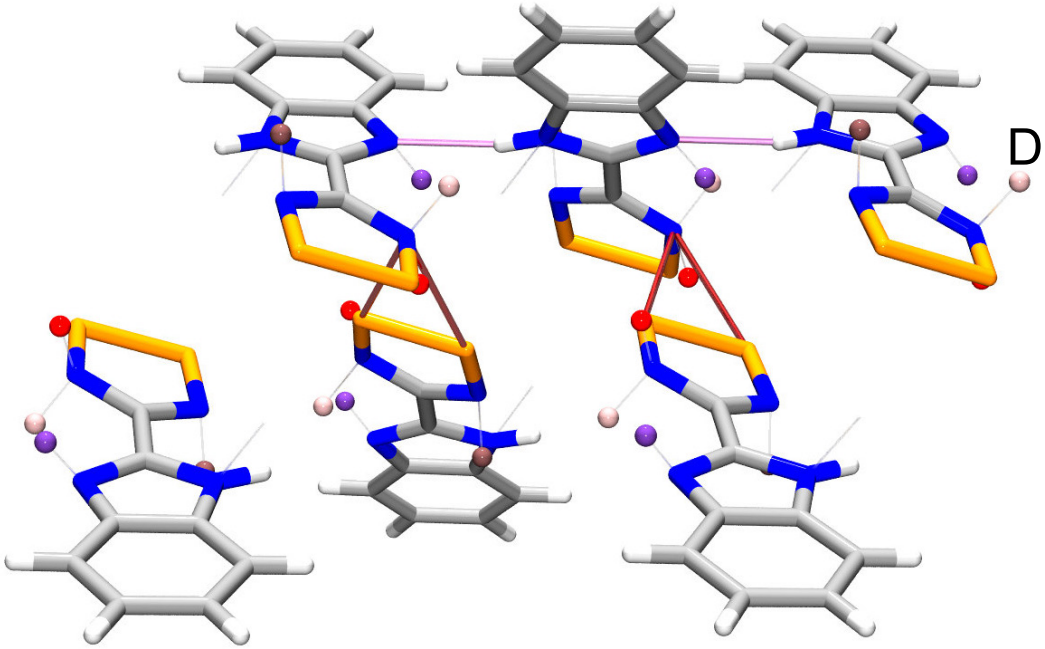

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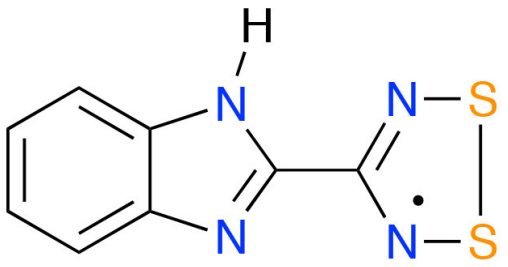

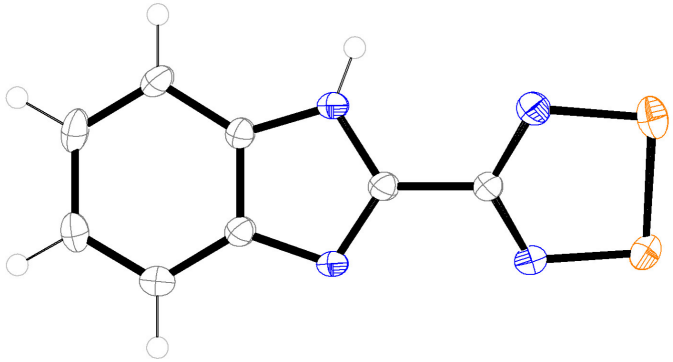

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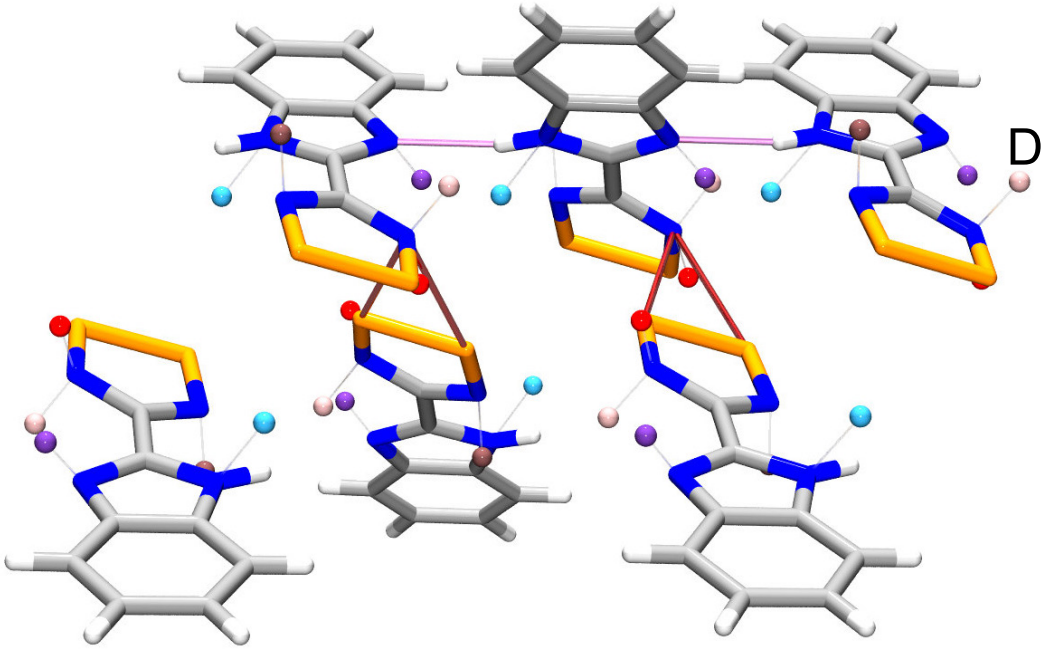

Where are the muons?

DFT using artificially-lightened H atom
→ +mu

site 1
site 2
site 3
site 4
site 5

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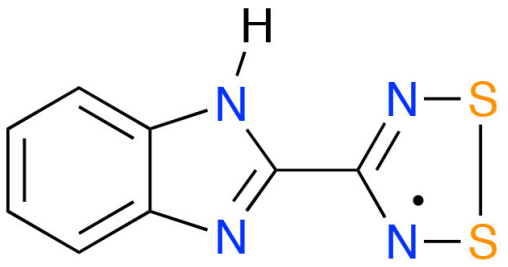
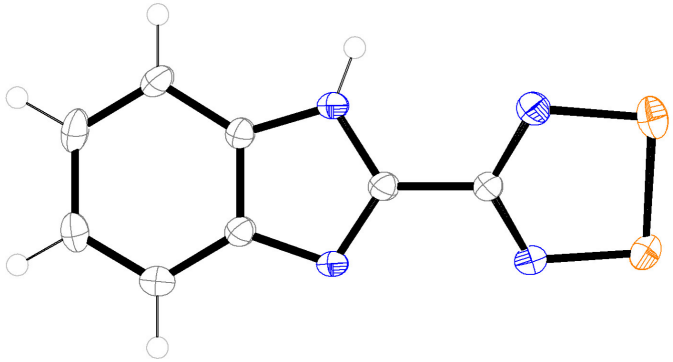
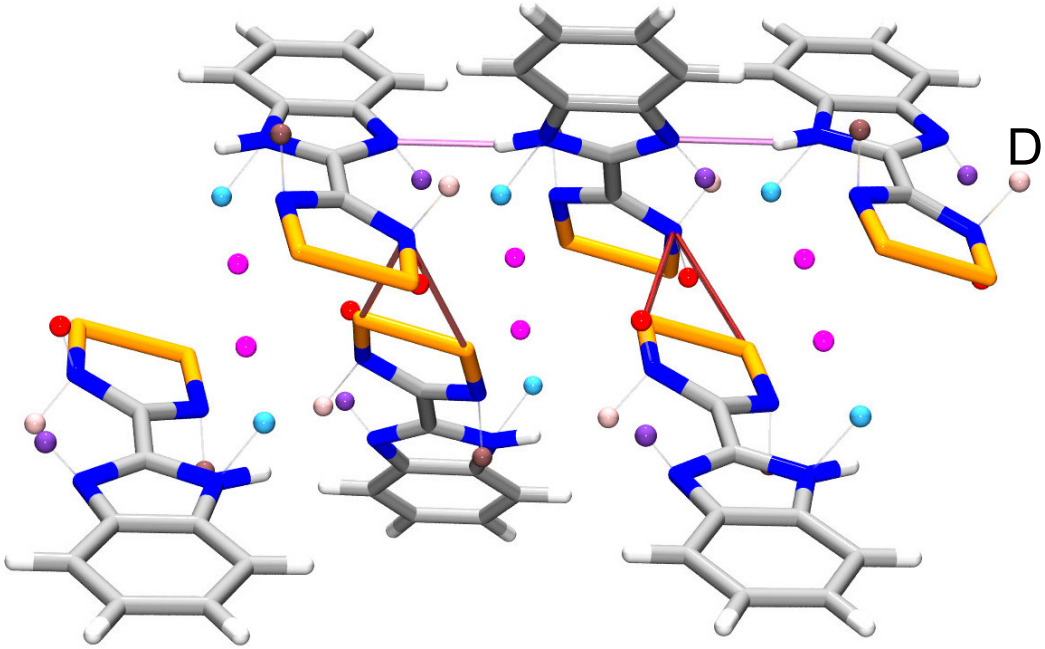




340 K



Where are the muons?

DFT using artificially-lightened H atom
→ +mu

site 1
site 2
site 3
site 4
site 5
site 6

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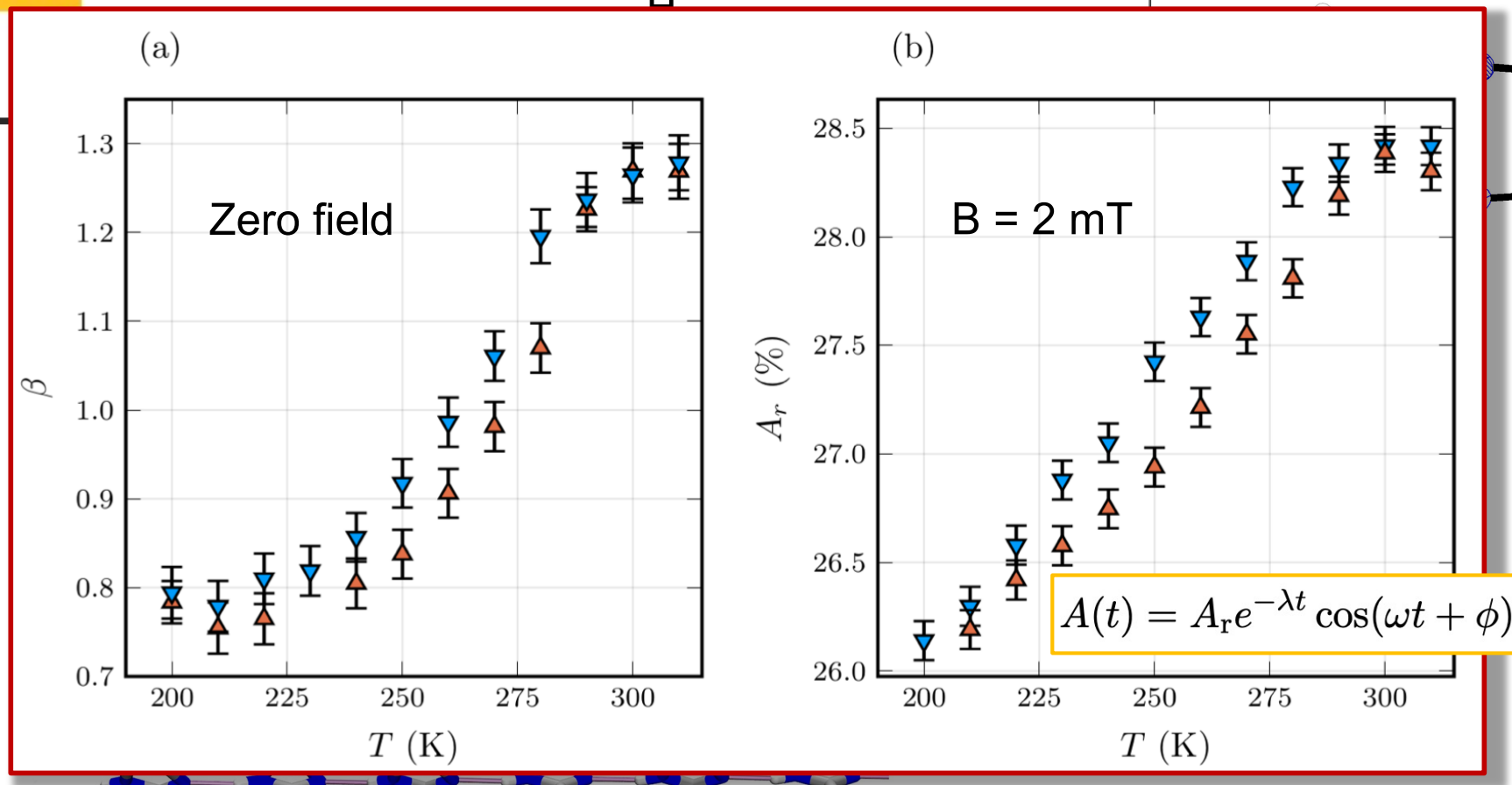

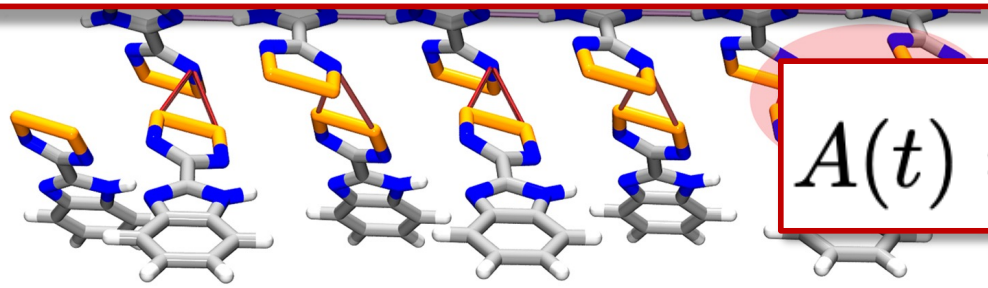

$$A(t) = A_r e^{-(\lambda t)^\beta} + A_b$$

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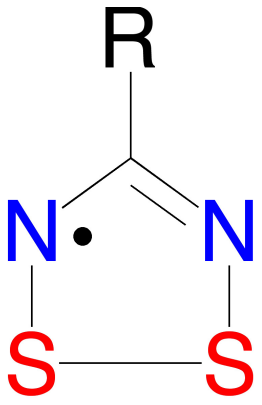
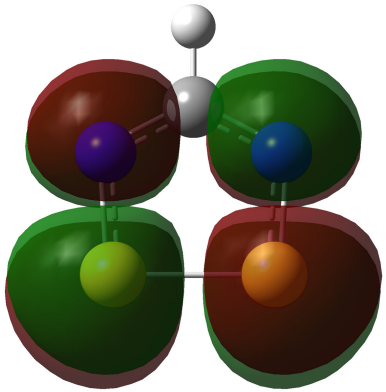
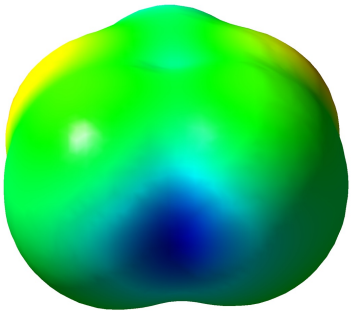
1,2,3,5-DTDA Electrostatics

Sigma-hole type feature & partial charge distribution

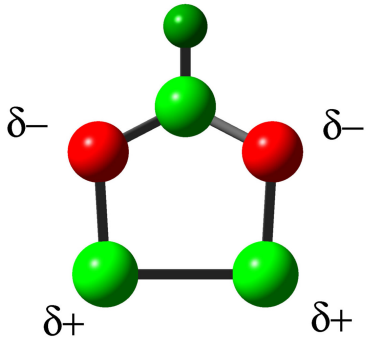




SOMO



ESP Surface



Charge Distribution

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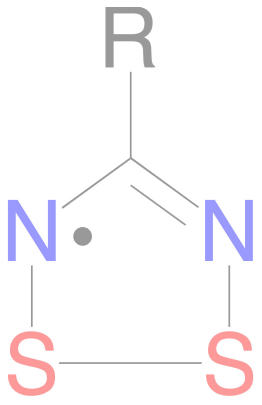
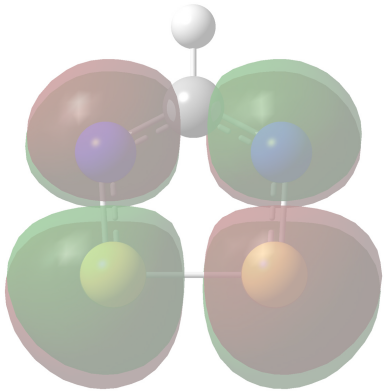
Spin Density: McConnel I Mech'm





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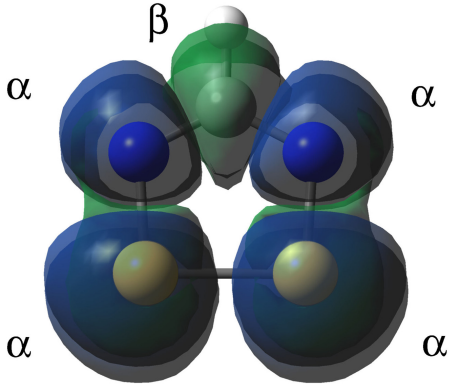
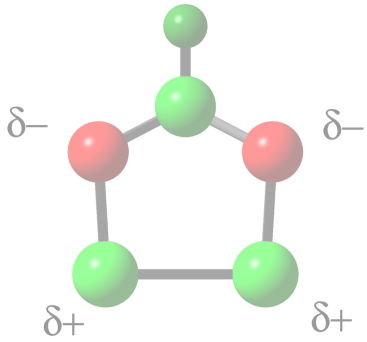
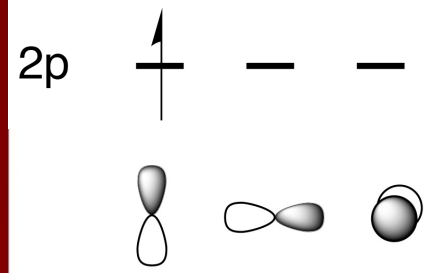


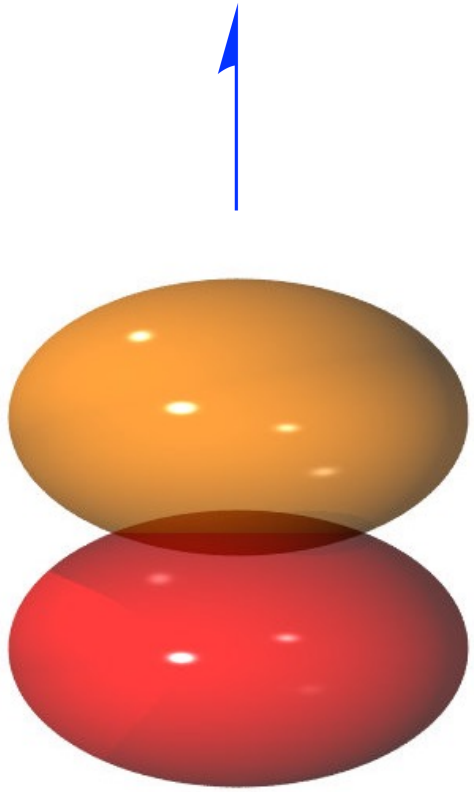
Spin Density



Charge Distribution

What is Spin Polarization?





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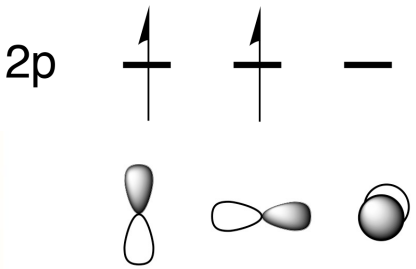

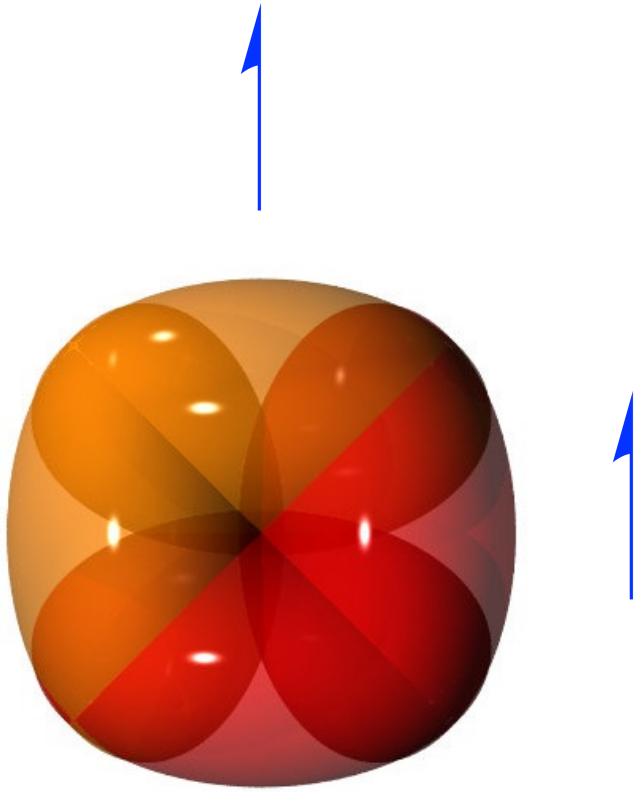

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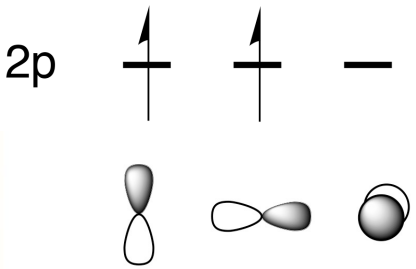

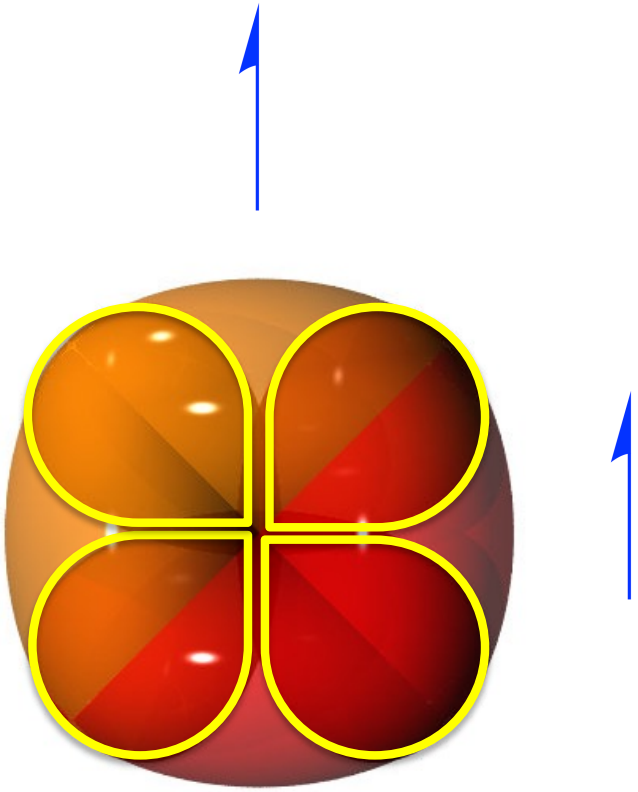

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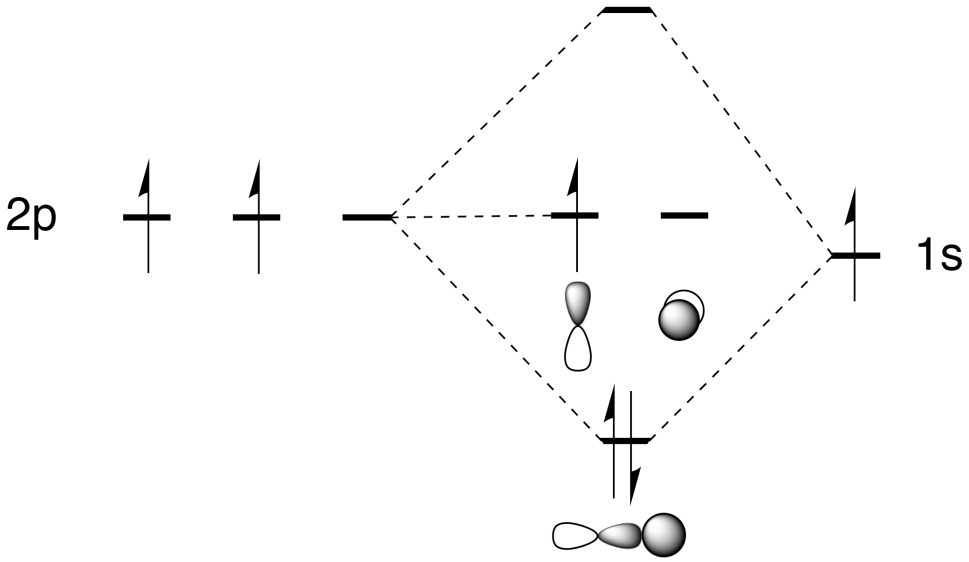

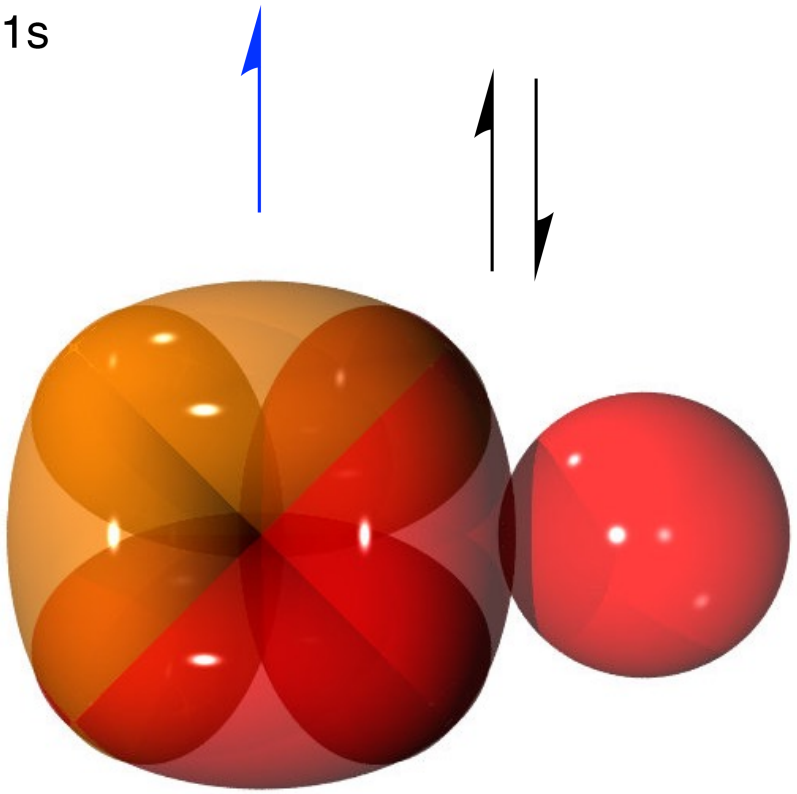

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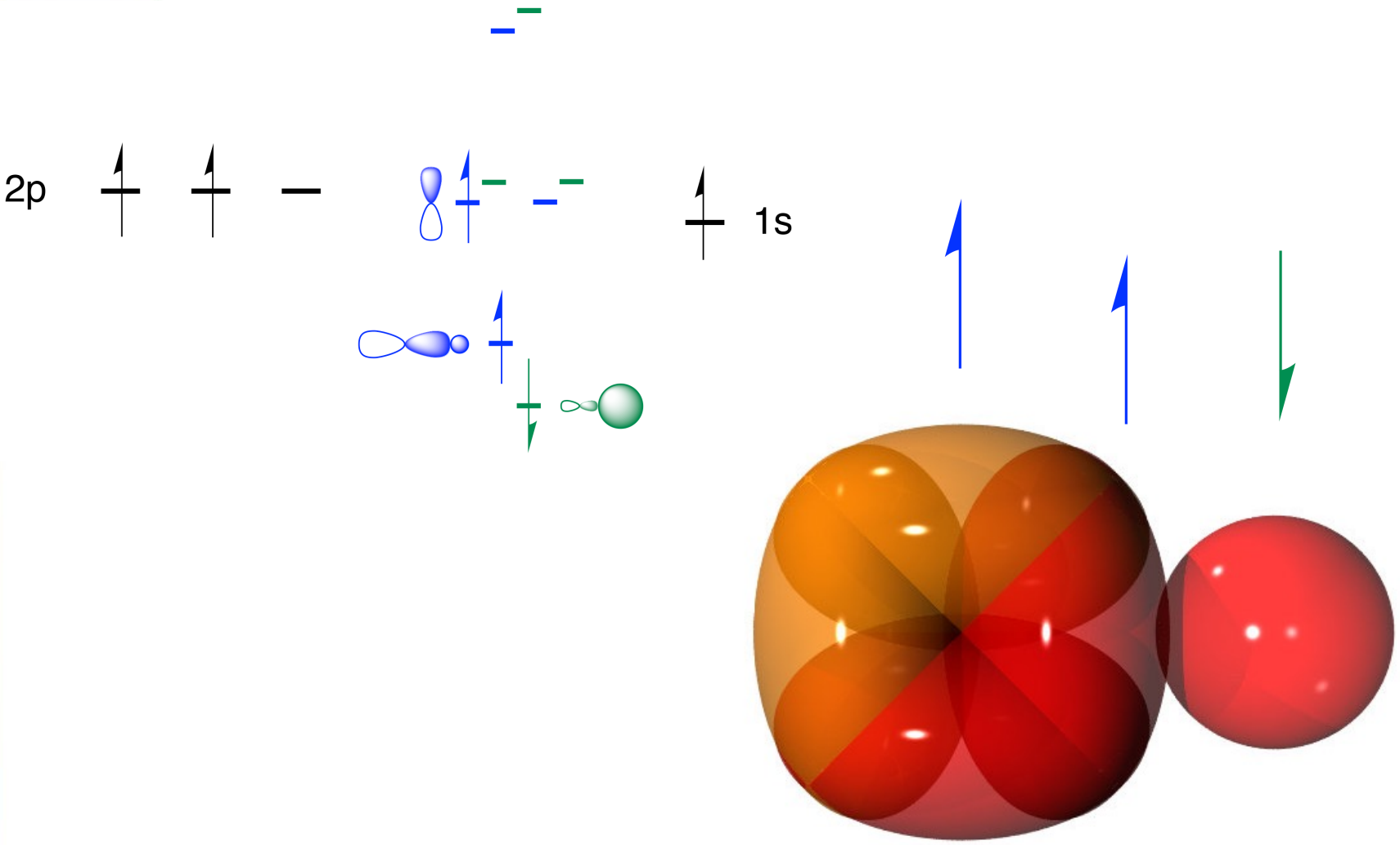

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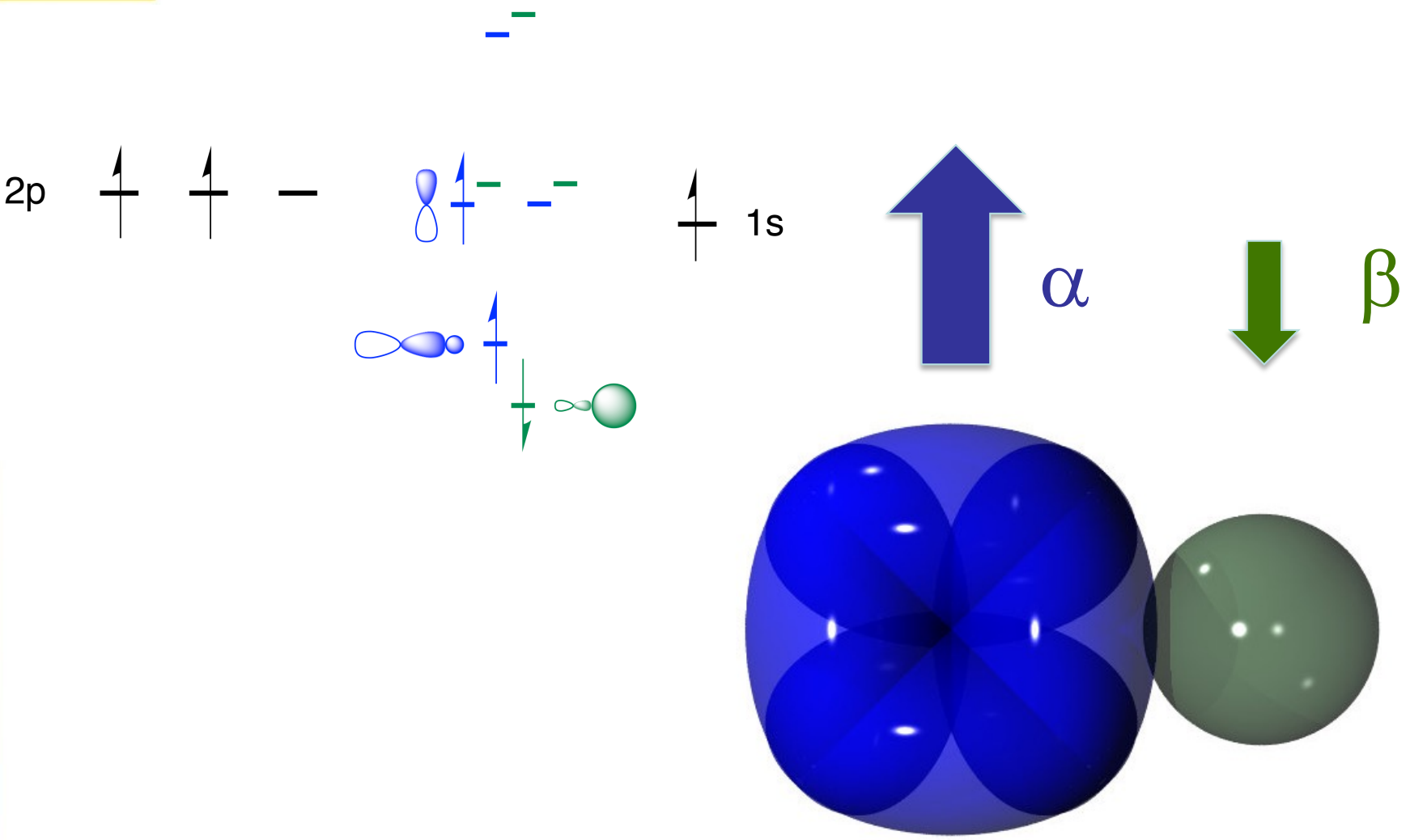

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Spin Density: McConnel I Mech'm

Ferromagnetism in Solid Free Radicals*

HARDEN M. MCCONNELL

Departments of Chemistry† and Physics, California Institute of Technology, Pasadena, California

(Received 5 June 1963)

THE paramagnetic resonance of picrylaminocarbazyl (PAC) and Wurster's blue perchlorate (WB) at very low temperatures (1.5°–4°K) has been studied by Edelstein and Mandel,[1] and they have suggested that these solid free radicals become ferromagnetic at sufficiently low temperatures. A recent single-crystal resonance study[2] of WB indicates that the elementary electronic excitations in this substance are triplet excitons, and that the resonance studied by Edelstein and Mandel in WB is very probably due to an impurity. However, the work of Edelstein and Mandel still raises the question of ferromagnetic interaction in PAC and in solid free radicals in general.

Present experimental evidence[2–5] indicates that the paramagnetic susceptibilities of *most* crystalline aromatic free radicals approach zero as $T \to 0$, when allowance is made for the impurity spins that are almost always present in such crystals. It is reasonable to assume that this tendency for the spins on adjacent free radicals in the crystal lattice to be antiparallel involves an exchange interaction similar to that appropriate to two weakly interacting hydrogen atoms, except that the exchange interaction between two aromatic rings is a many-center problem. If we consider only two-center exchange integrals, then the exchange interaction between two aromatic radicals A and B can be approximated by the Hamiltonian

$$\mathcal{H}^{AB} = -\sum_{ij} J_{ij}^{AB} \mathbf{S}_i^A \cdot \mathbf{S}_j^B, \qquad (1)$$

where $\mathbf{S}_i^A$ is the π-electron spin on Atom i of Molecule A, and $\mathbf{S}_j^B$ is the π-electron spin on Atom j of Molecule B. Equation (1) can also be written in the form

$$\mathcal{H}^{AB} = -\mathbf{S}^A \cdot \mathbf{S}^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B, \qquad (2)$$

where $\mathbf{S}^A$ and $\mathbf{S}^B$ are the total spin operators for A and B, and ρ_i^A and ρ_j^B are the π-spin densities[6] on Atoms i and j of Molecules A and B. The dominant tendency towards antiparallel spin coupling in solid free radicals can be ascribed to the facts that the spin densities ρ_i^A and ρ_j^B are usually positive, and the largest exchange integrals J_{ij}^{AB} are negative for aromatic molecules that are pancaked on top of one another in crystals.[2,7]

The purpose of this note is to point out that in certain aromatic and olefinic free radicals (especially odd-alternant radicals) there are large positive *and* negative atomic π-spin densities, and that it is quite possible that in special cases these radicals may pancake on top of one another in the crystal lattice so that atoms of positive spin density are exchange coupled most strongly to atoms of negative spin density in neighboring molecules. This gives a ferromagnetic exchange interaction favoring parallel (total) spin angular momentum on neighboring molecules. The chemical structure of PAC indicates that there may indeed be negative spin densities on some atoms in this substance. It would therefore appear that a search for ferromagnetic interactions in solid free radicals might well be directed towards radicals with large negative spin densities.

* Sponsored by the U. S. Atomic Energy Commission, and the National Science Foundation.

† Contribution No. 2987.

[1] A. S. Edelstein and M. Mandel, J. Chem. Phys. **35,** 1130 (1961).

[2] H. M. McConnell, D. Pooley, and A. Bradbury, Proc. Natl. Acad. Sci. (U.S.) **48,** 1480 (1962); D. D. Thomas, H. Keller, and H. M. McConnell, J. Chem. Phys. (to be published).

[3] R. S. Rhodes, J. H. Burgess, and A. S. Edelstein, Phys. Rev. Letters **6,** 462 (1961).

[4] D. B. Chesnut and W. D. Phillips, J. Chem. Phys. **35,** 1002 (1961).

[5] D. B. Chesnut and P. Arthur, Jr., J. Chem. Phys. **36,** 2969 (1962).

[6] H. M. McConnell, J. Chem. Phys. **28,** 1188 (1958).

[7] In the unlikely event that the nearest-neighbor aromatic free radicals were oriented so that the rings (and π orbitals) were perpendicular to one another, then the J_{ij}^{AB} would be positive, but very small.

McConnel, H. M. *J. Chem. Phys*

Yoshizawa, K.; Hoffman, R. *J. Am. Chem. Soc.*, **1995**, *117*, 6921.

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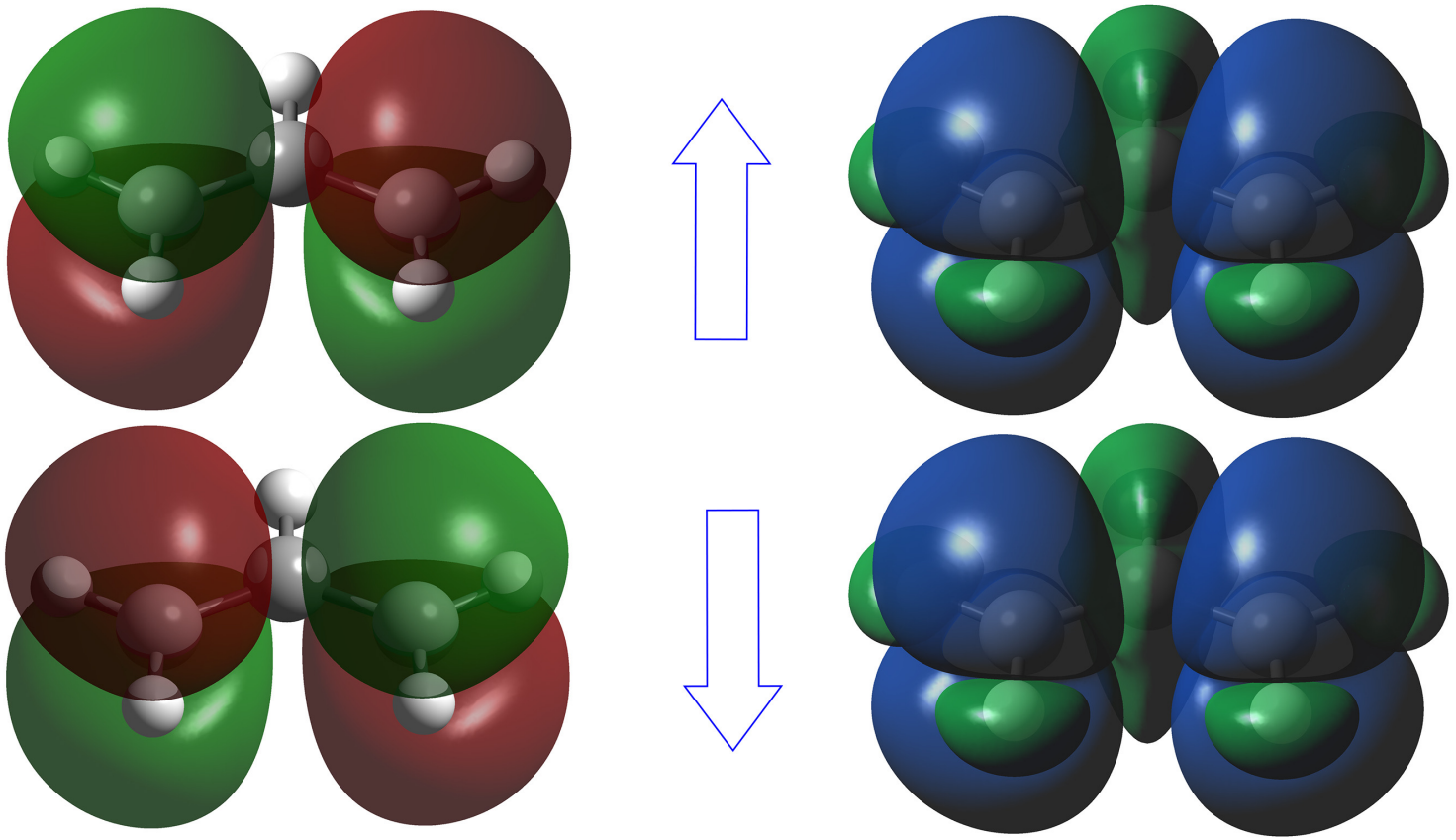
Spin Density: McConnel I Mech'm

Allyl radical

AFM coupling



$S = 0$

McConnel, H. M. *J. Chem. Phys.*, **1963**, *39*, 1910.
Yoshizawa, K.; Hoffman, R. *J. Am. Chem. Soc.*, **1995**, *117*, 6921.

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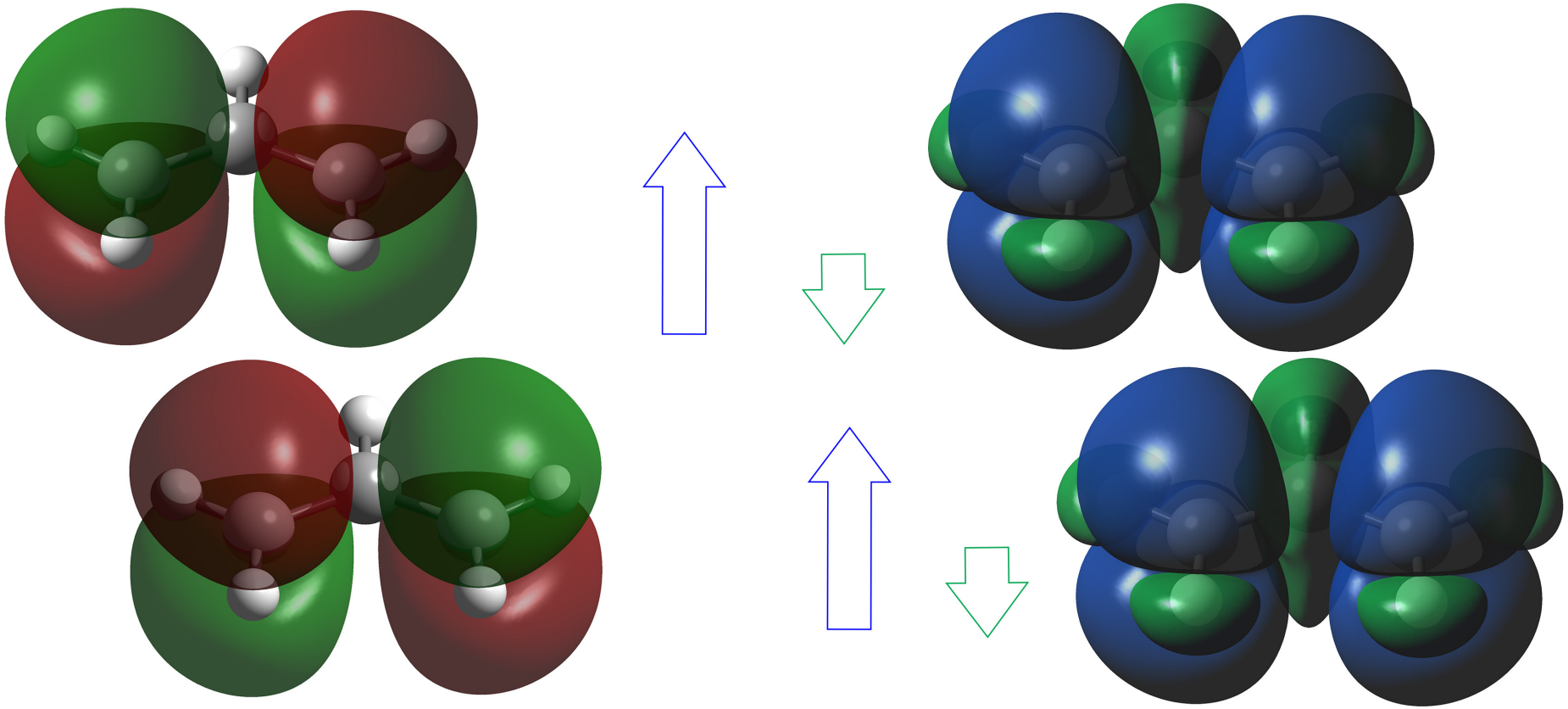
Spin Density: McConnel I Mech'm

Allyl radical

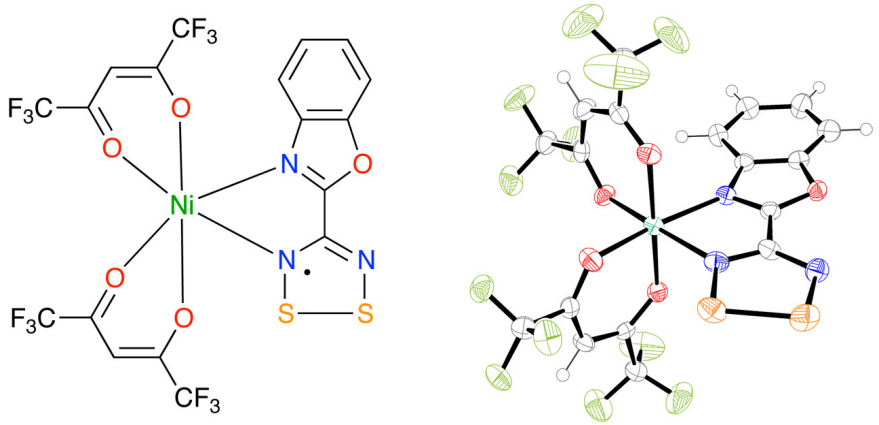
FM coupling



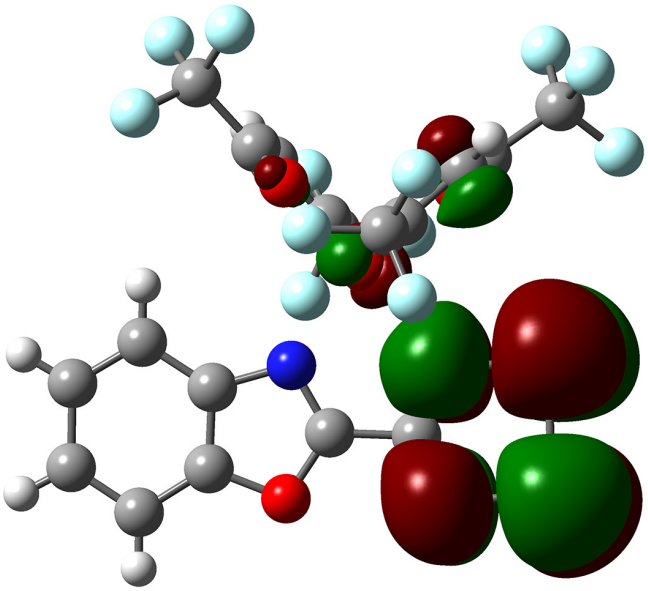
$S = 1$

McConnel, H. M. *J. Chem. Phys.*, **1963**, *39*, 1910.
Yoshizawa, K.; Hoffman, R. *J. Am. Chem. Soc.*, **1995**, *117*, 6921.

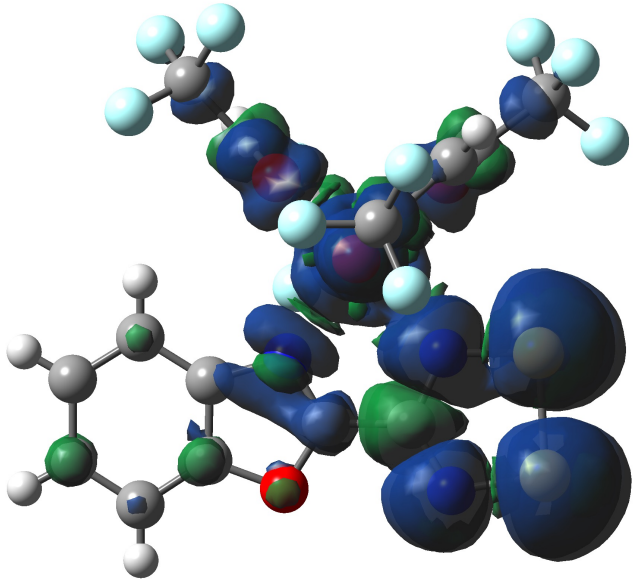
Ni boaDTDA: Heisenberg Model



Ni(II) complex S_T = 3/2
FM intermolecular interactions



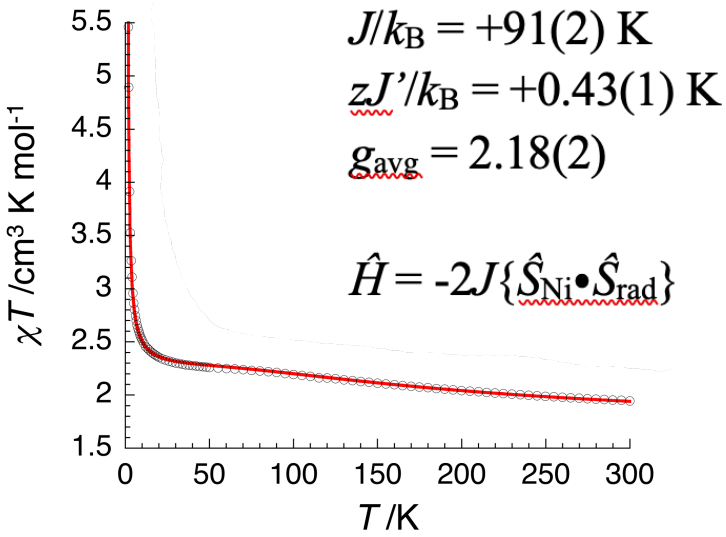
SOMO (highest occupied)



Spin Density

Fatila, E. M.; Clérac, R.; Jennings, M.; Preuss, K. E. *Chem. Commun.,* **2013**, *49*, 9431.

Ni boaDTDA: Heisenberg Model

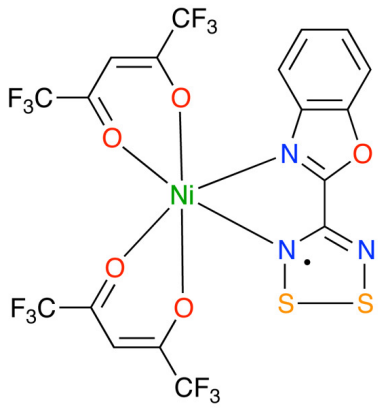


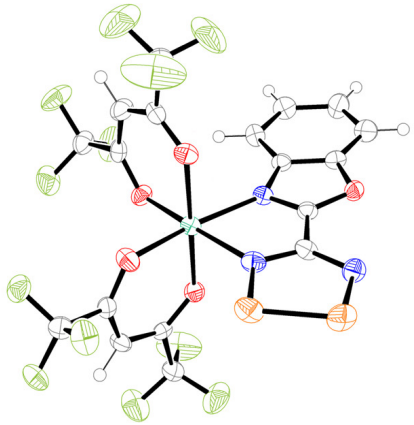
$J/k_B = +91(2)$ K

$zJ'/k_B = +0.43(1)$ K

$g_{avg} = 2.18(2)$

$\hat{H} = -2J\{\hat{S}_{Ni} \bullet \hat{S}_{rad}\}$





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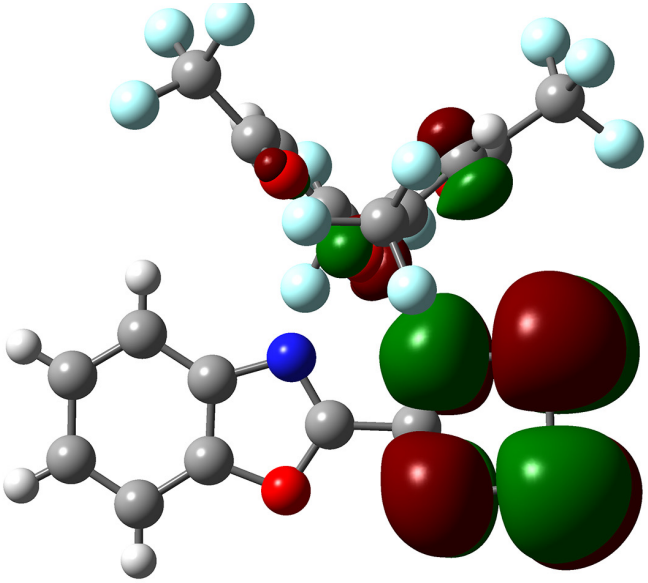

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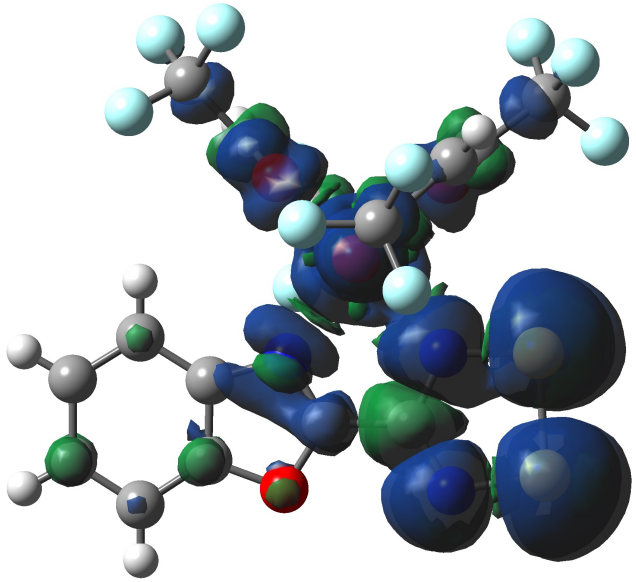

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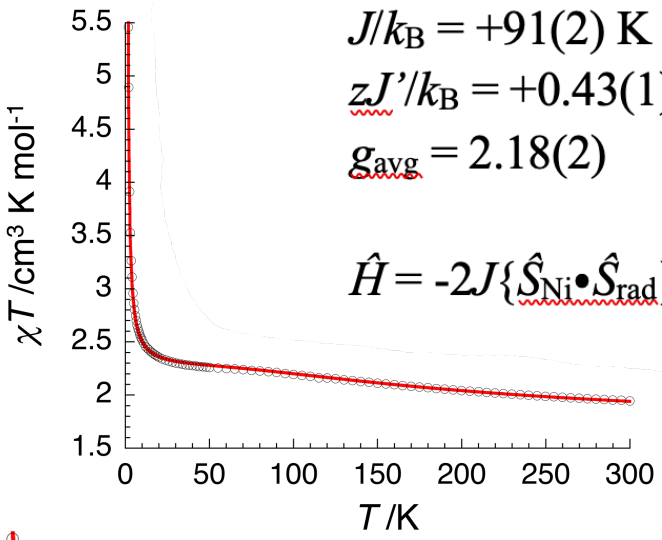

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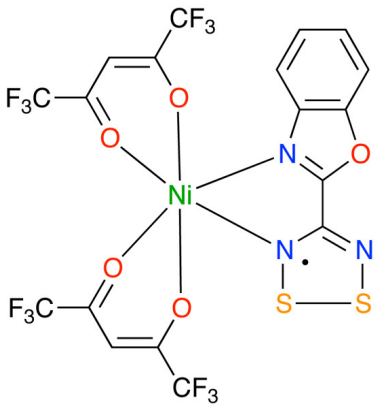

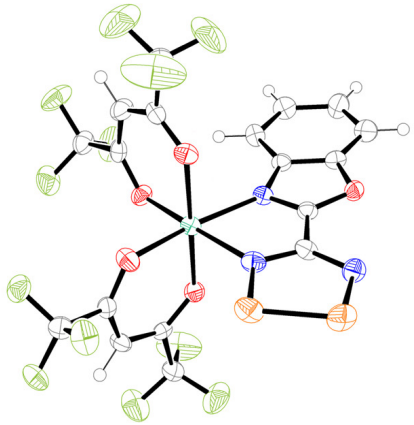

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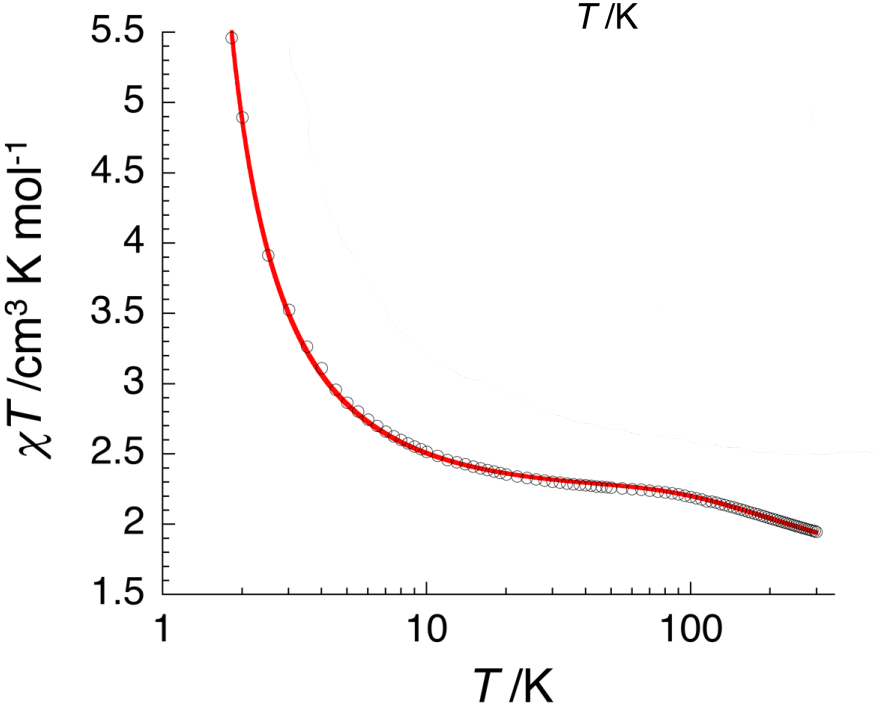

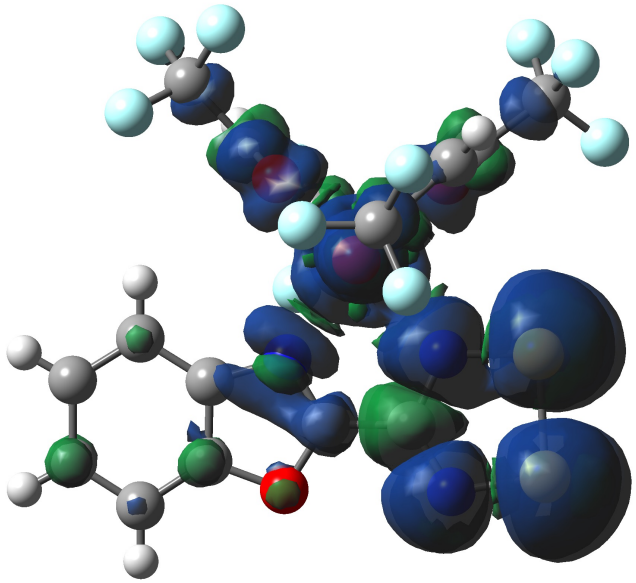

Spin Density

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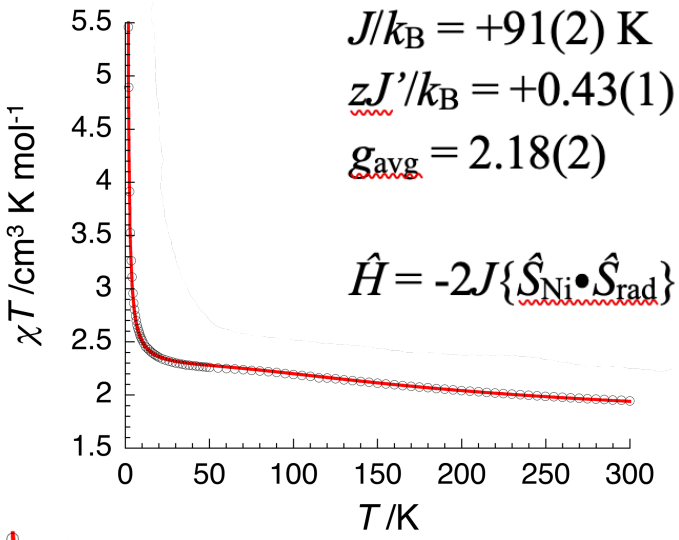

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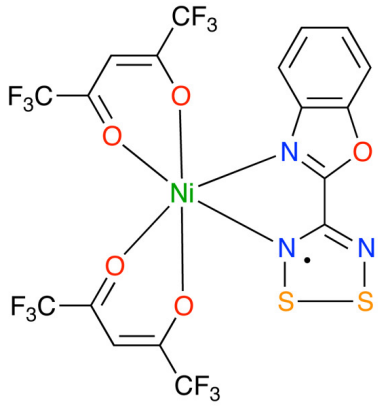

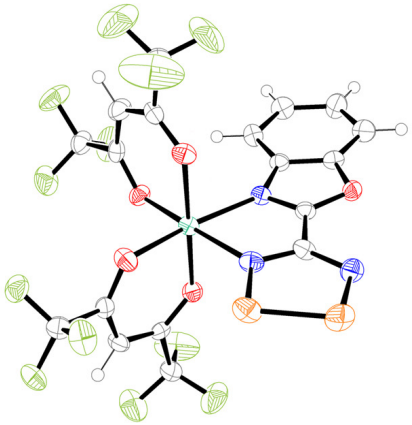

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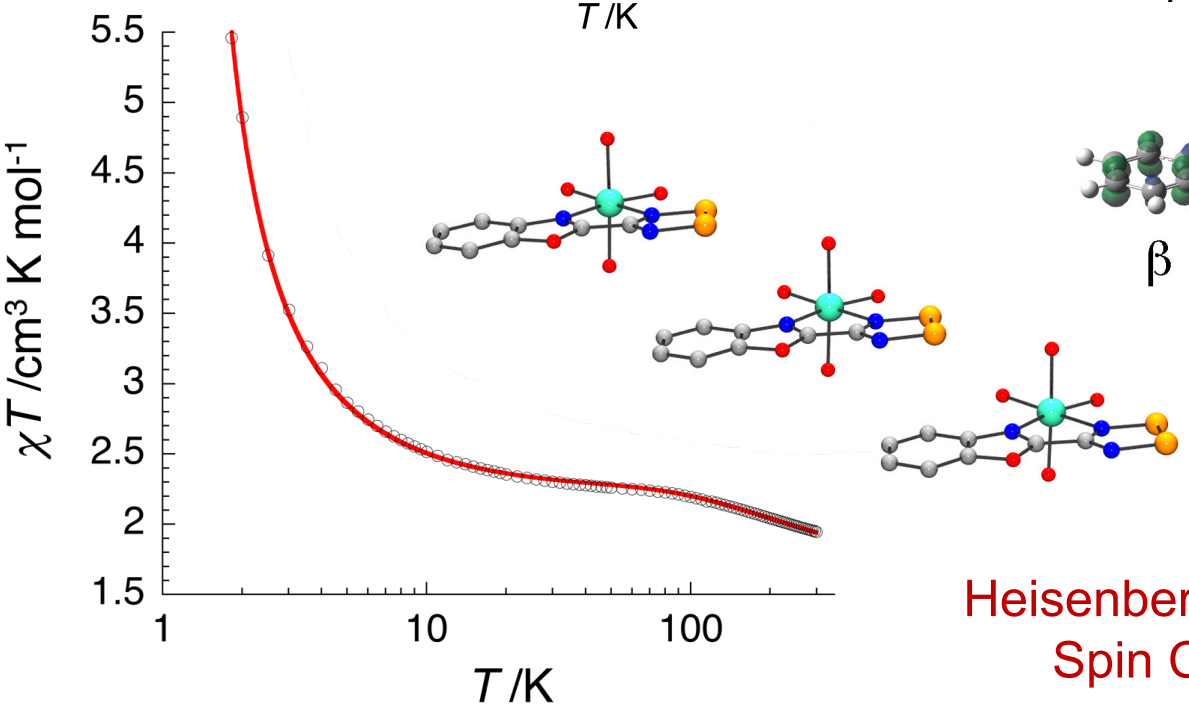

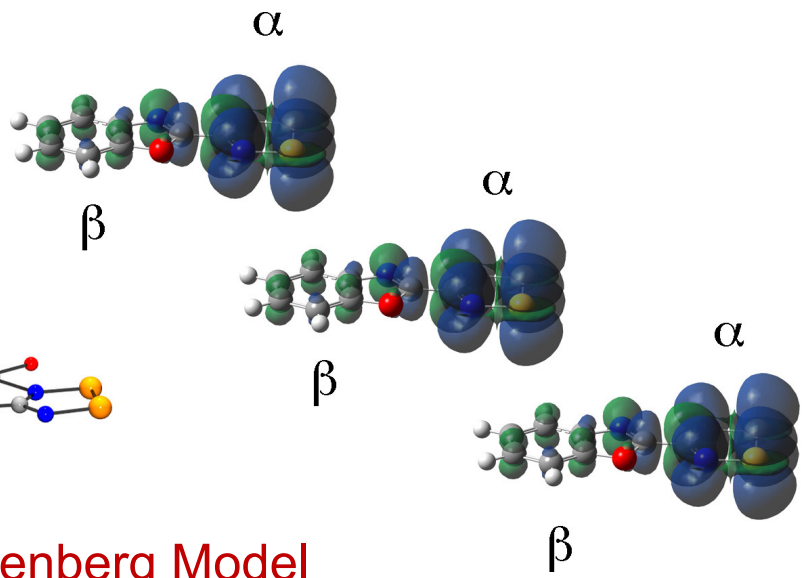

Heisenberg Model
Spin Chain

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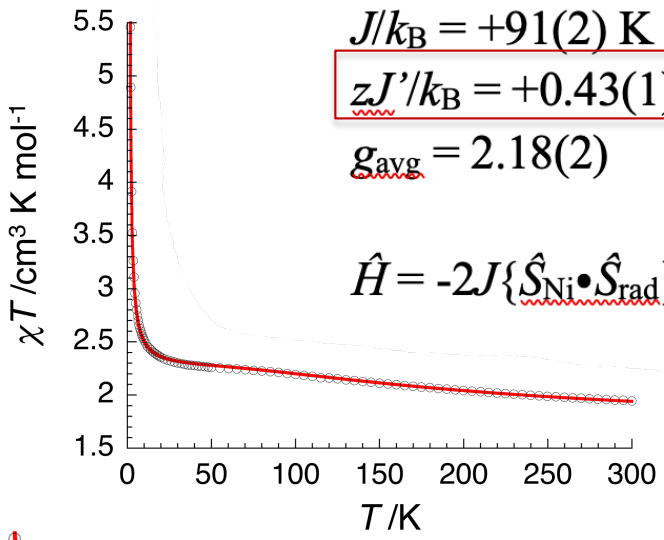
Ni boaDTDA: Heisenberg Model



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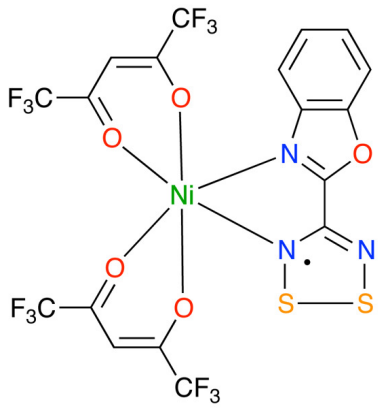
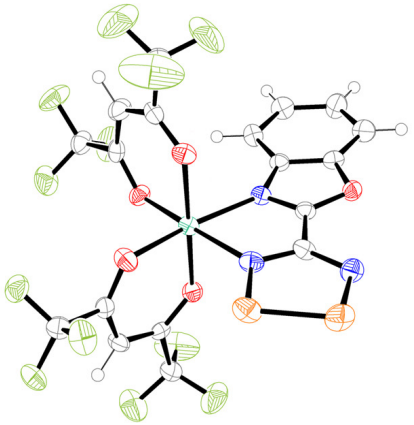
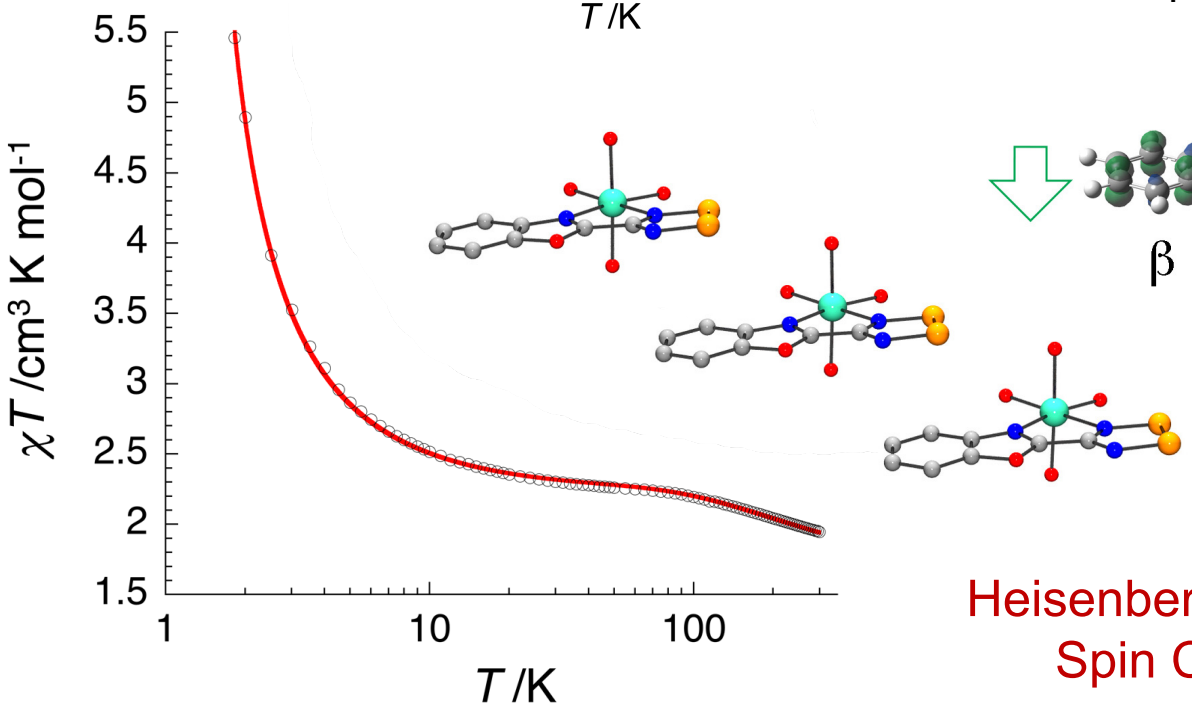
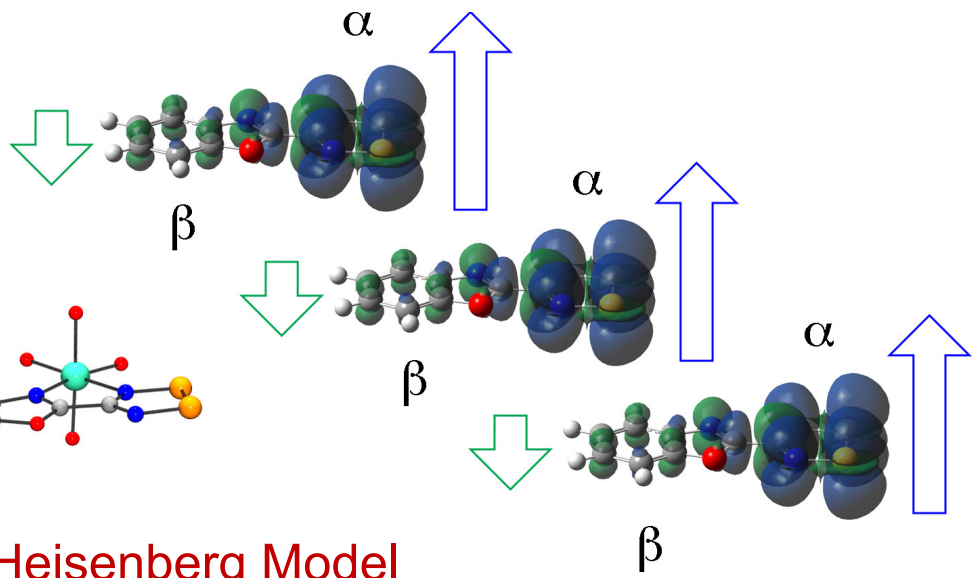




Ni(II) complex $S_T = 3/2$

FM intermolecular interactions





Heisenberg Model
Spin Chain

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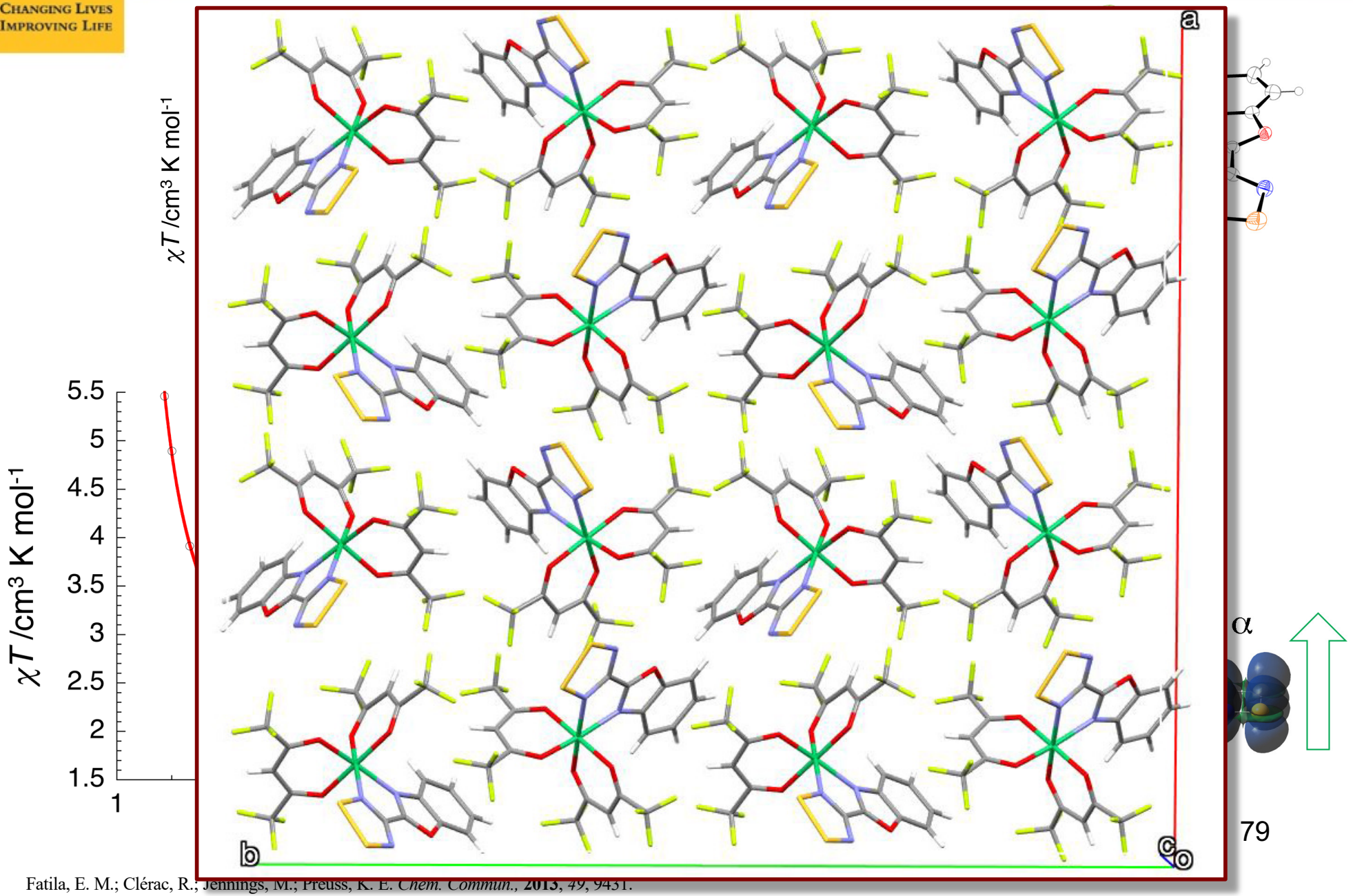
Ni boaDTDA: Heisenberg Model



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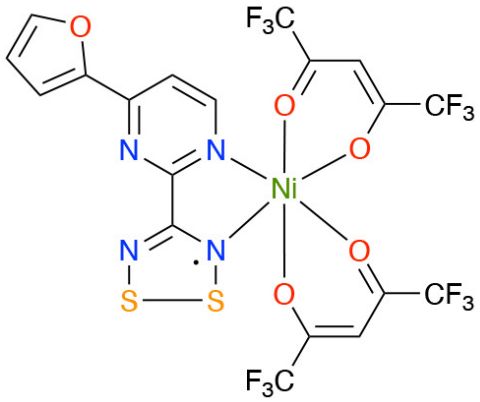
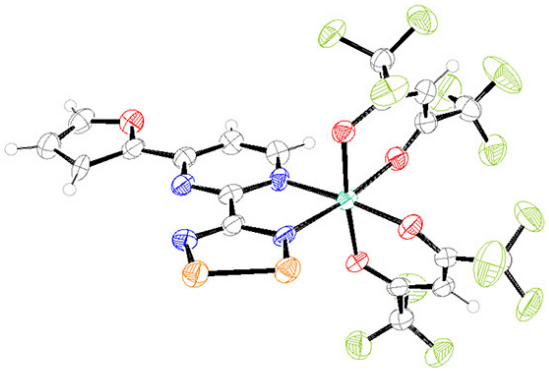
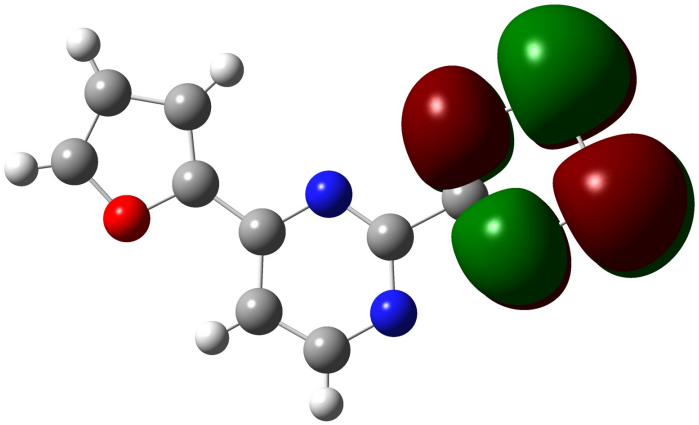
Ni fpymDTDA: Heisenberg Model



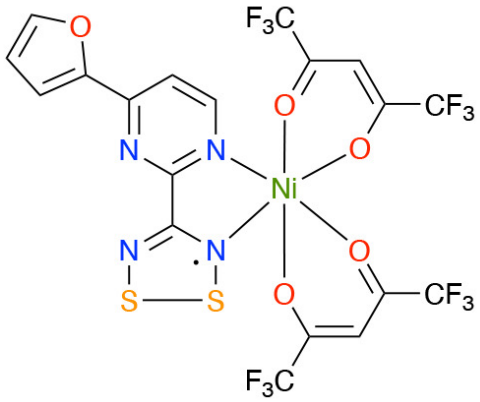


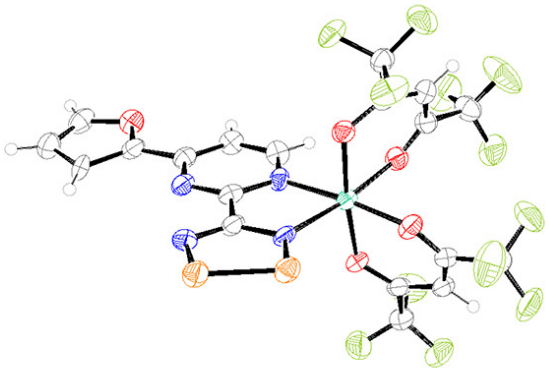
Maahs, A. C.; Borg, G. C; Ghazzali, M.; Soldatov, D. V.; Rouzières, M.; Clérac, R.; Preuss, K. E. *Chem. Eur. J.* **2024**, *30*, e202403220.

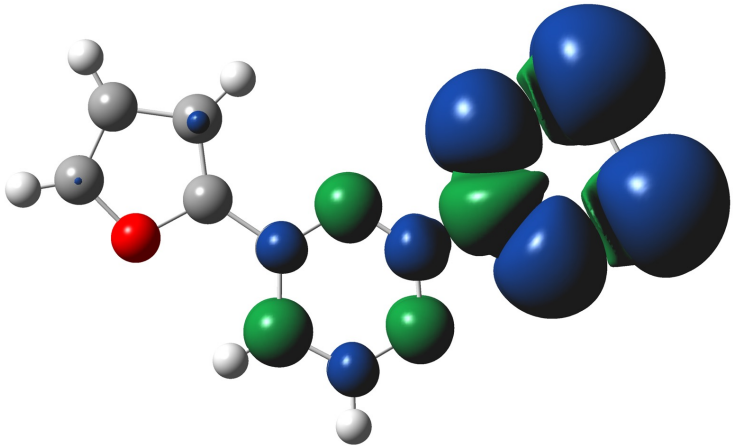
Ni fpymDTDA: Heisenberg Model



SOMO







Spin density

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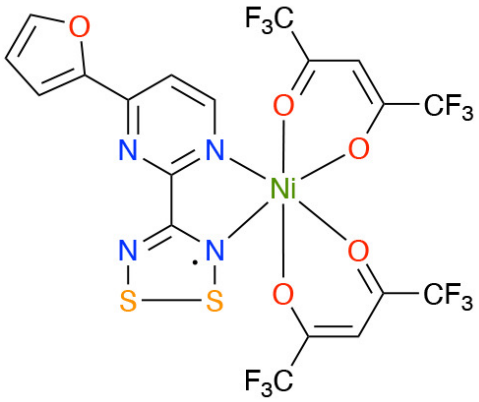

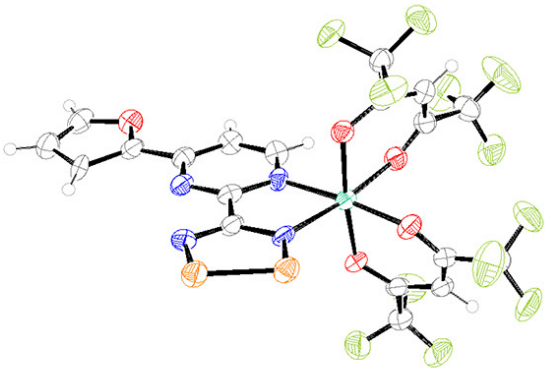

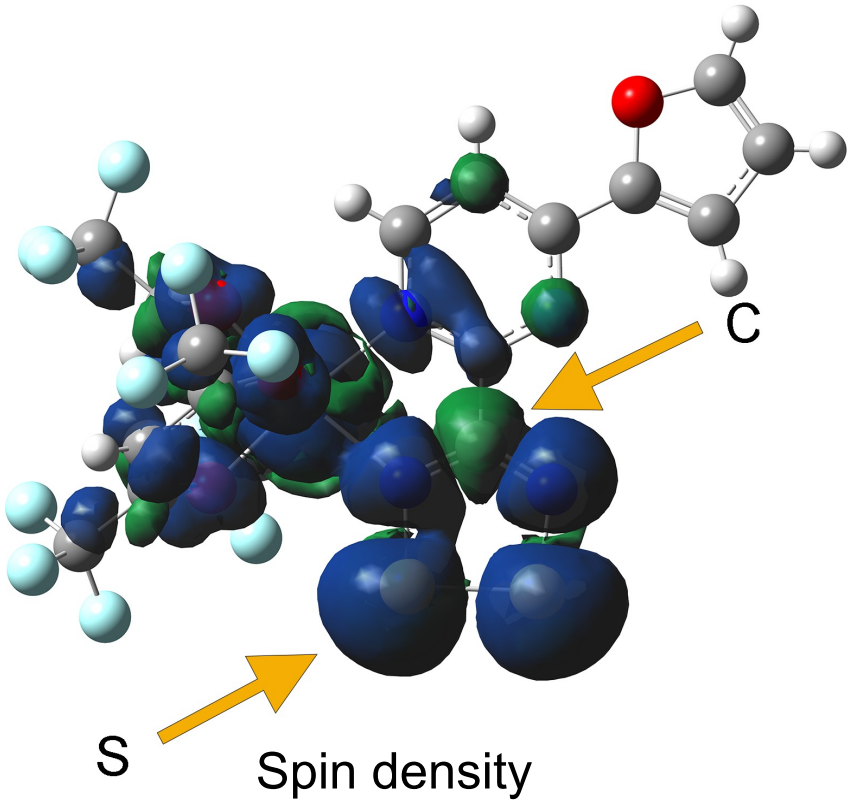

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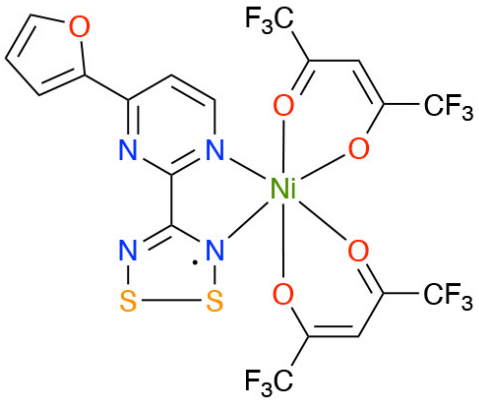

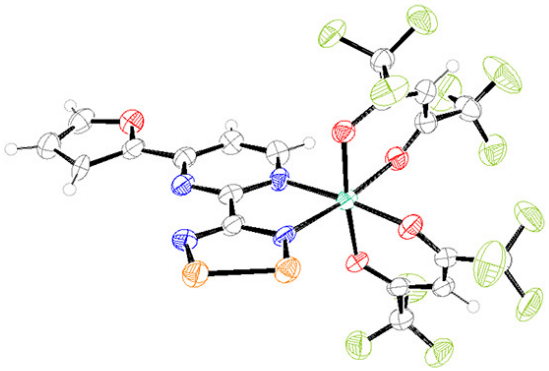

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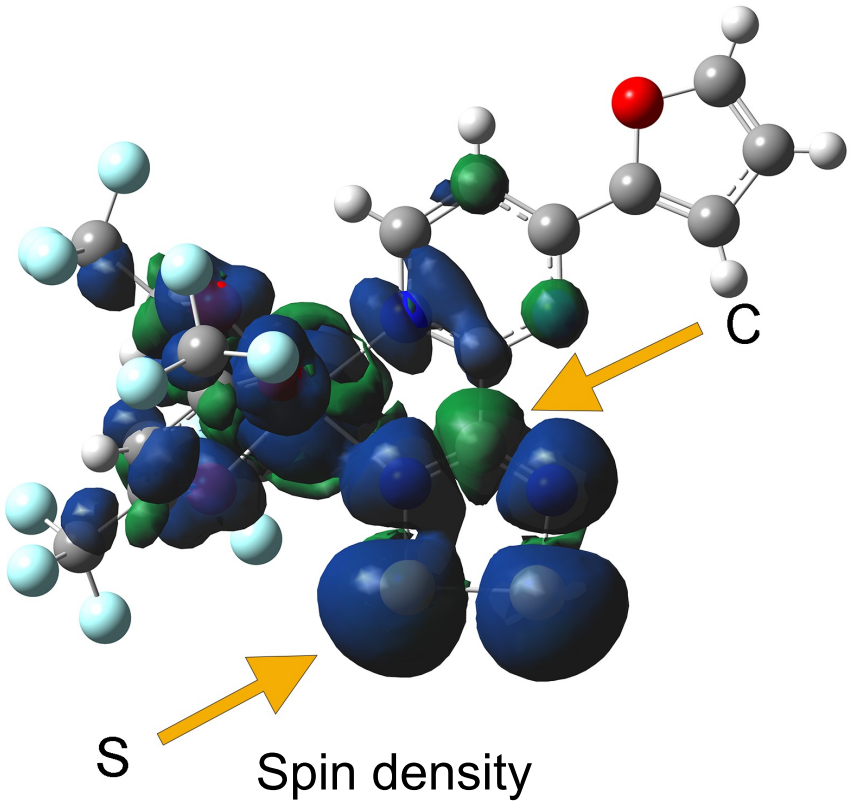
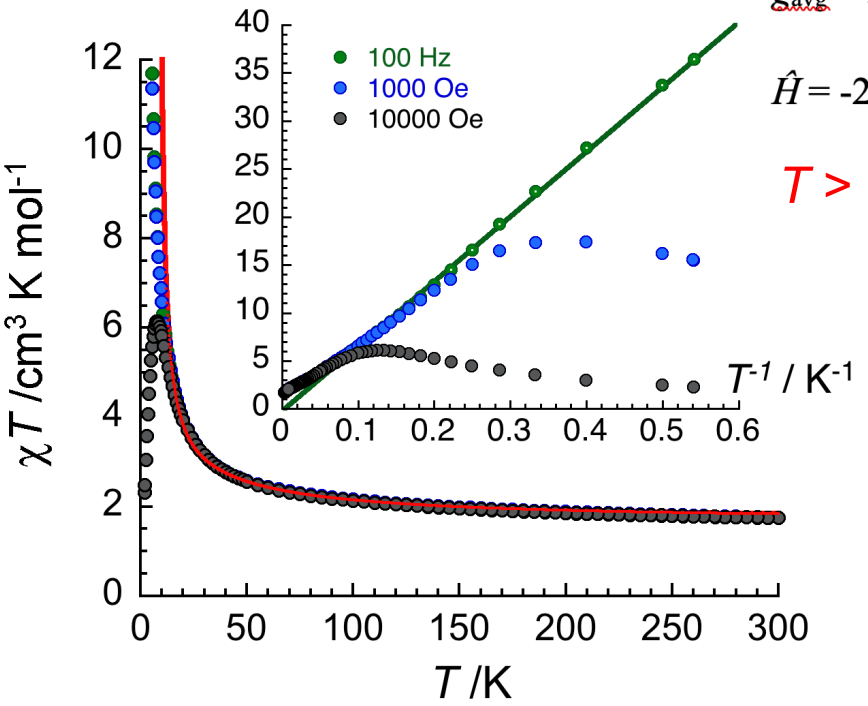
$T > 15$ K





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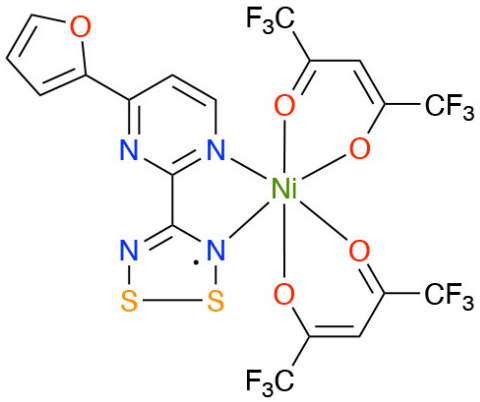
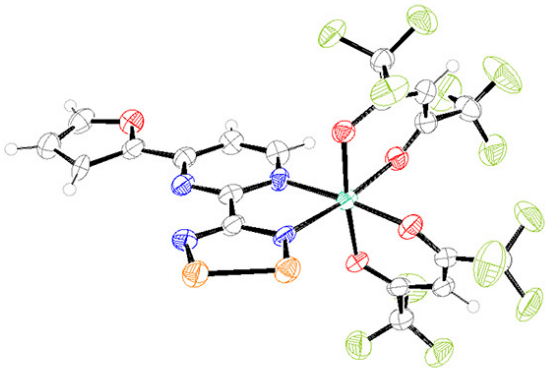
Ni fpymDTDA: Heisenberg Model

T < 15 K

χT strongly field-dependent





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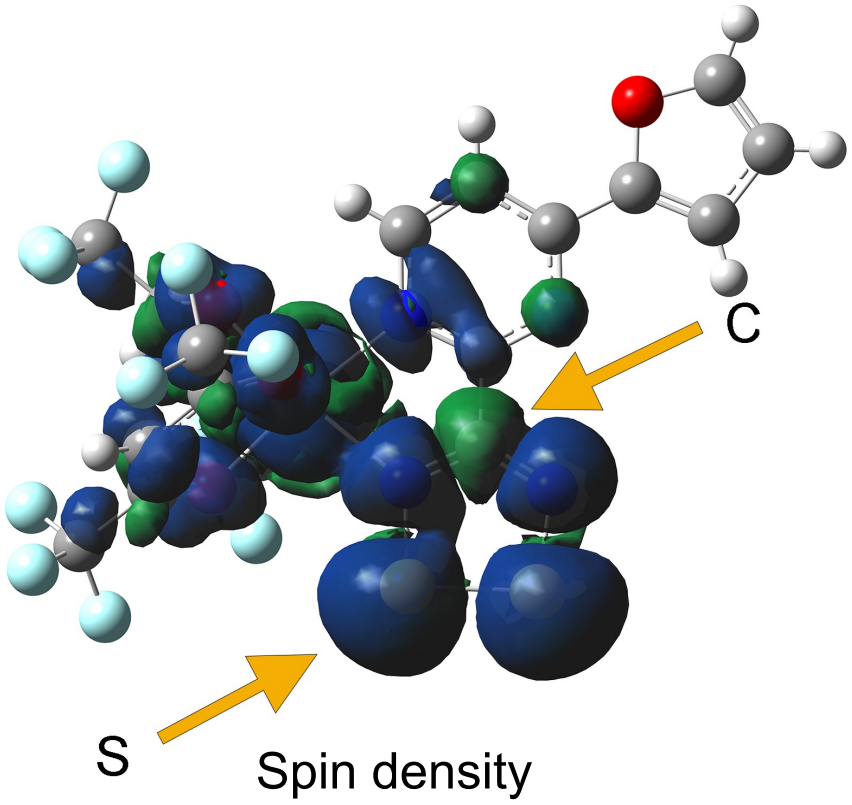

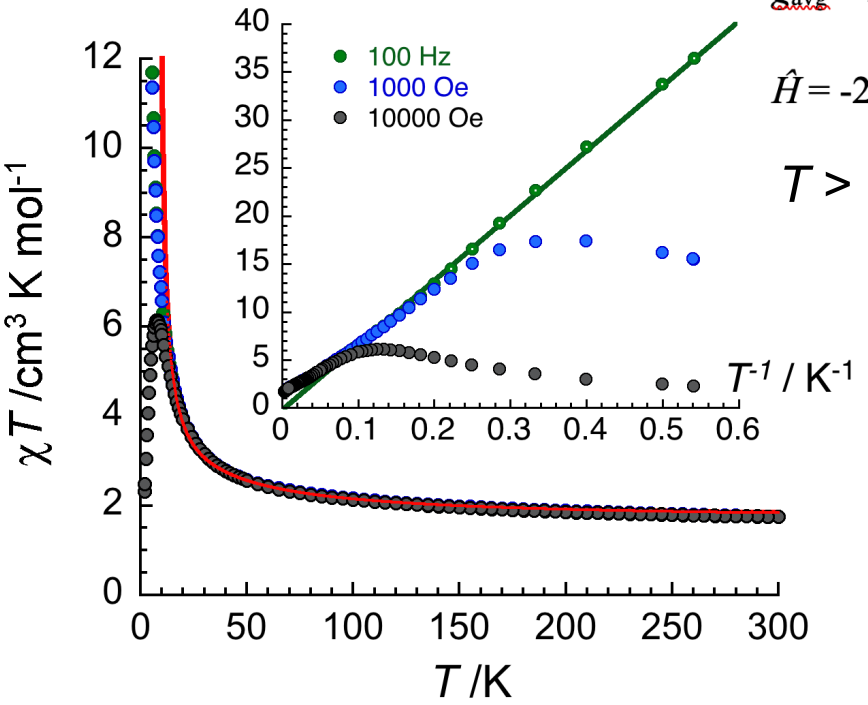

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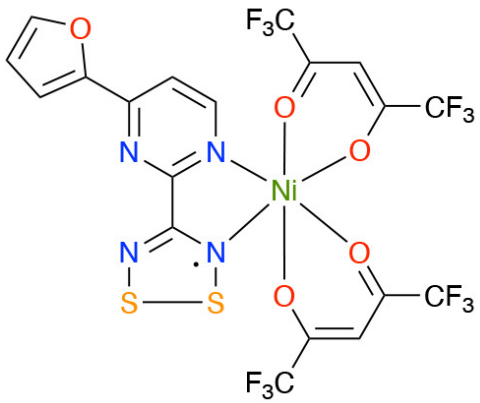
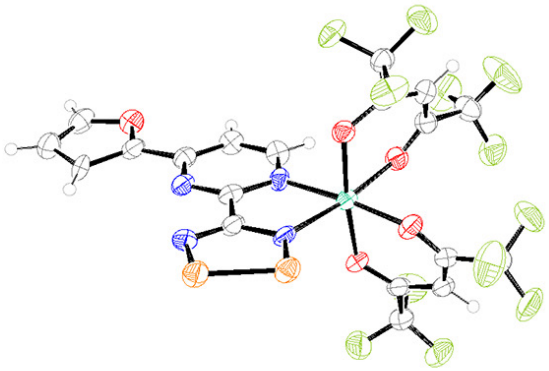
Ni fpymDTDA: Heisenberg Model

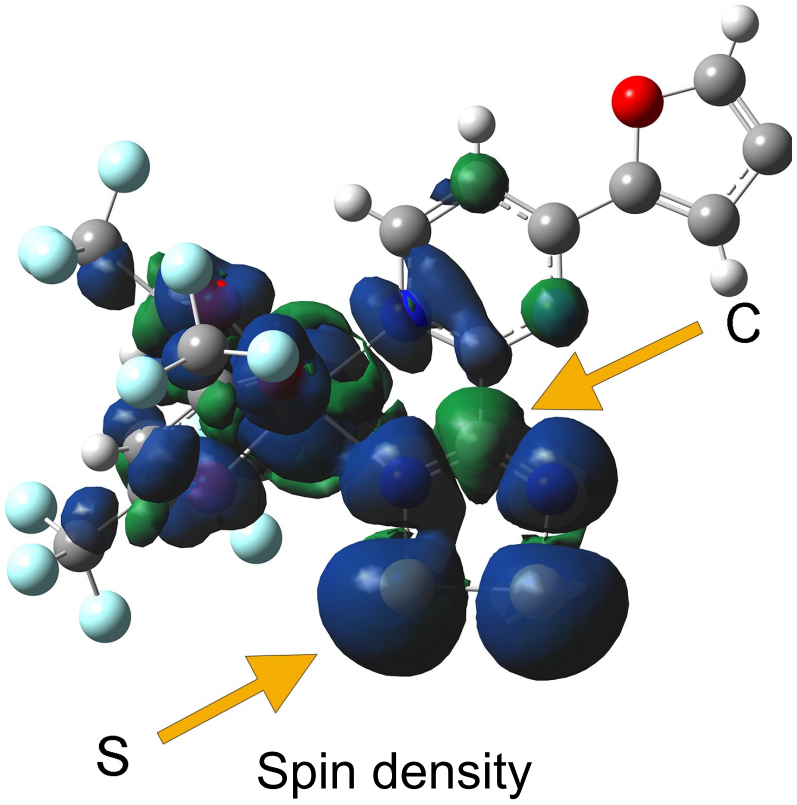
Heisenberg Spin Chain

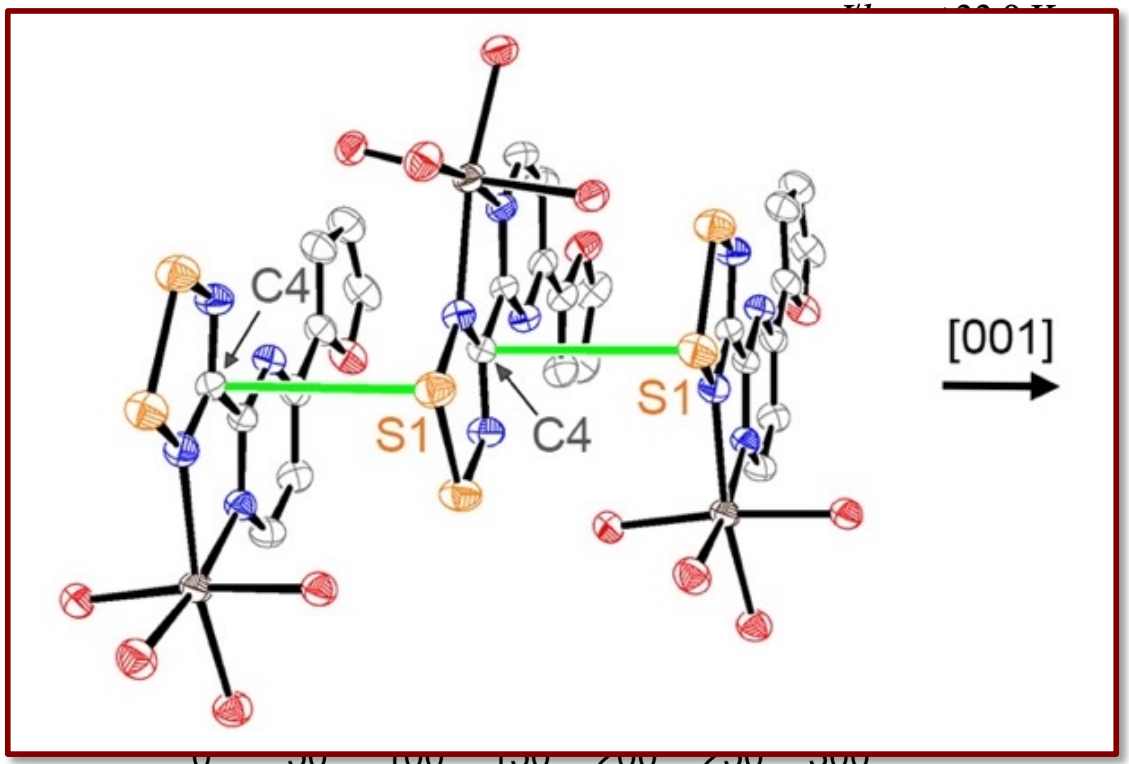
$T < 15$ K

$$\hat{H} = -2J_{\text{eff}} \sum_{-\infty}^{+\infty} \vec{S}_{\text{T},i} \vec{S}_{\text{T},i+1}$$









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Ni fpymDTDA: Heisenberg Model

Heisenberg Spin Chain

$T < 15$ K

$$\hat{H} = -2J_{\text{eff}} \sum_{-\infty}^{+\infty} \vec{S}_{\text{T},i} \vec{S}_{\text{T},i+1}$$

Fisher model

$$\frac{\chi T}{C} = \frac{2\xi}{l} \approx \frac{4J_{\text{eff}} S_T^2}{k_B T}$$

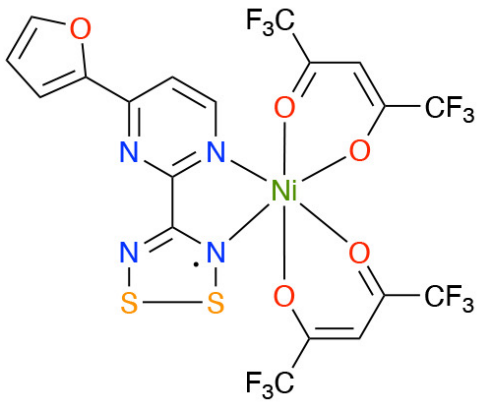
correlation length ξ

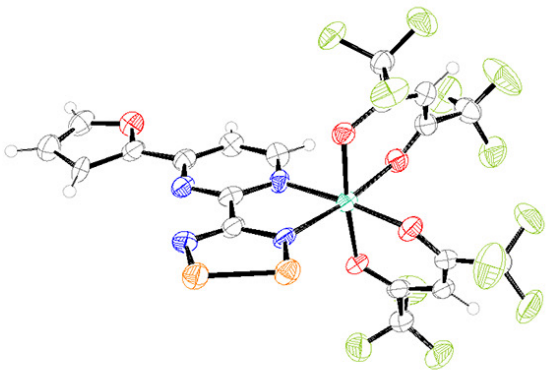
$4J_{\text{eff}}S_T^2/k_B = 62.6/C$

$C = 1.67$ cm^3 Kmol^{-1}

$J_{\text{eff}}/k_B = +4.5$ K

Isotropic (classical) Heisenberg spins



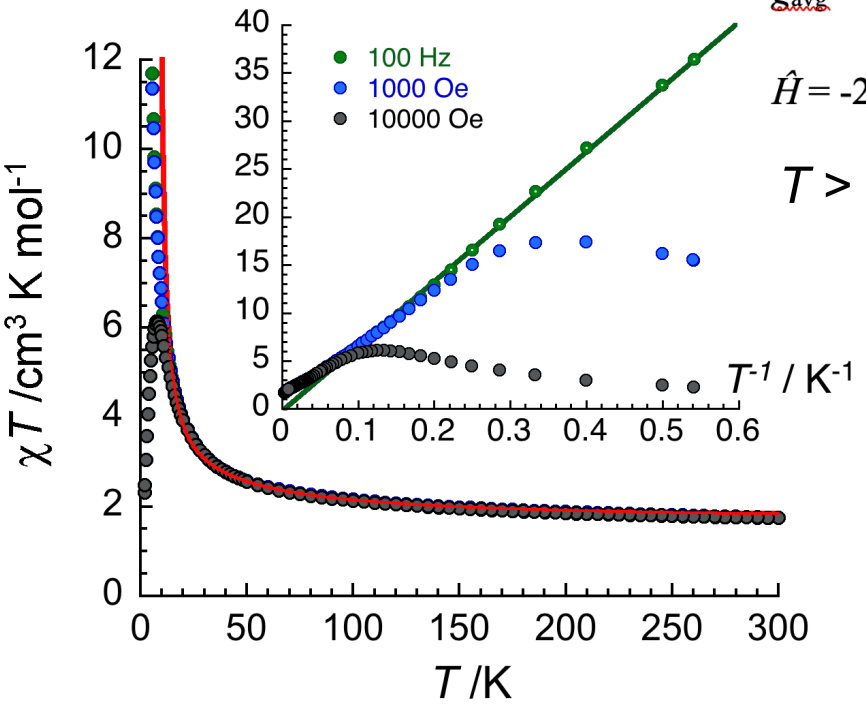


Ni(II) complex $S_T = 3/2$
FM intermolecular interactions

$J/k_B = +33.9$ K
$zJ'/k_B = +3.3$ K
$g_{avg} = 2.22$

$\hat{H} = -2J\{\hat{S}_{Ni} \bullet \hat{S}_{rad}\}$

$T > 15$ K



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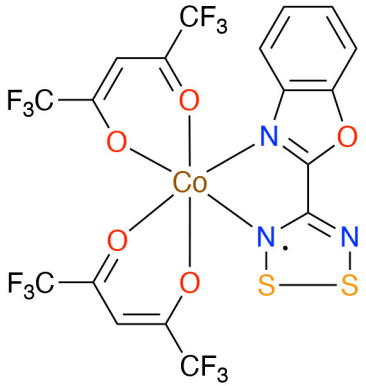
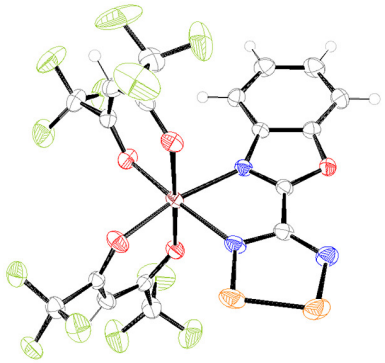
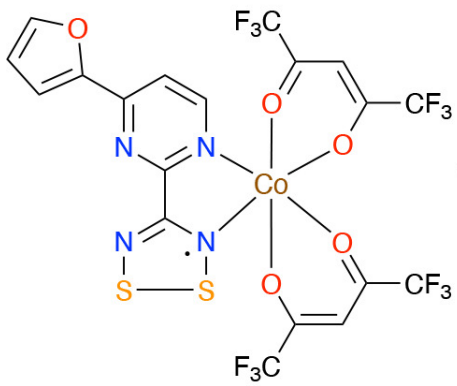
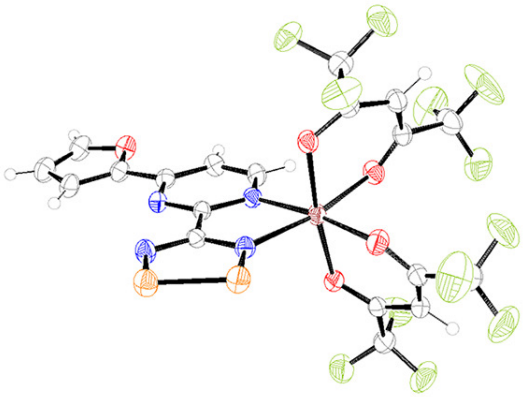
Co boaDTDA vs. Co fpymDTDA









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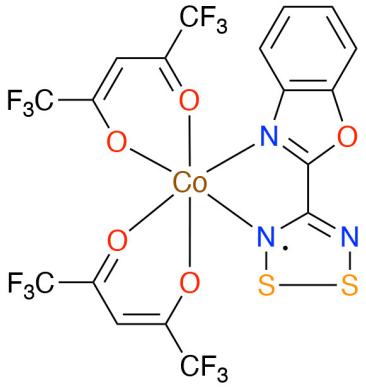
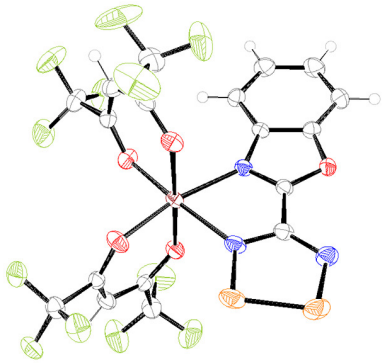
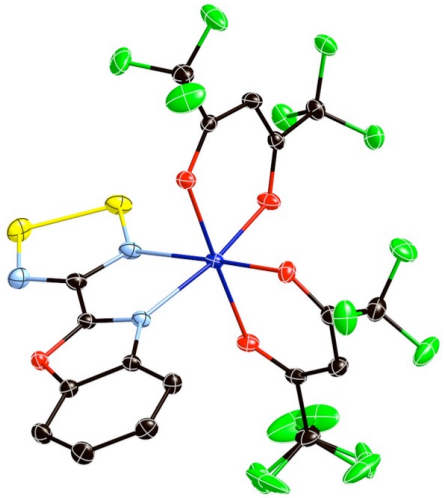
Co boaDTDA: FM Coupling

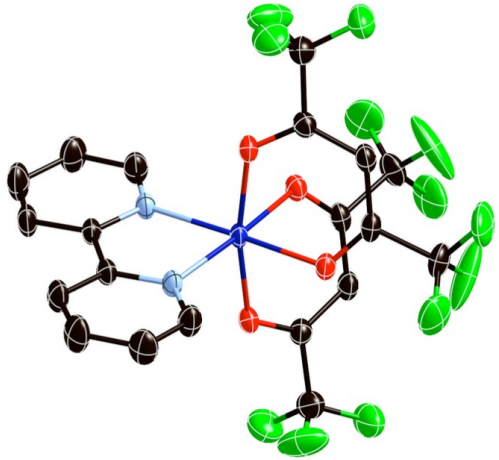




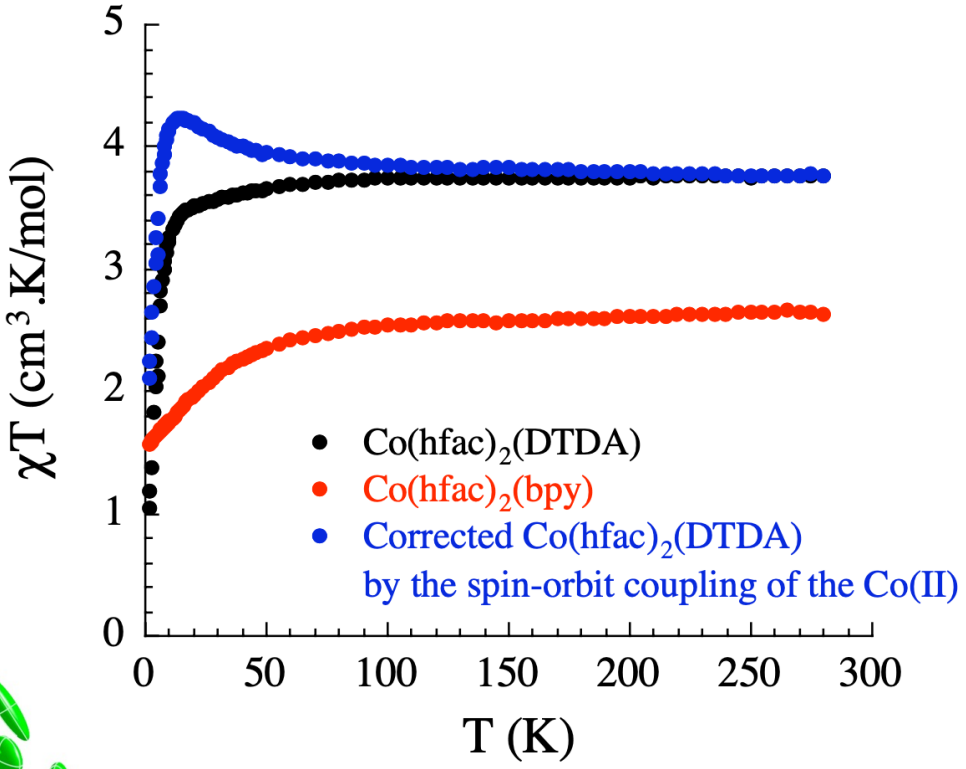
hs-Co(II) complex $S_T = 2$
FM intermolecular interactions



Co(hfac)$_2$(DTDA)



Co(hfac)$_2$(bpy)



$J/k_B = +9.5(8)$ K

$zJ'/k_B = -0.26(3)$ K

$g_{avg} = 2.46(5)$

$\hat{H} = -2J\{\hat{S}_{Co} \bullet \hat{S}_{rad}\}$

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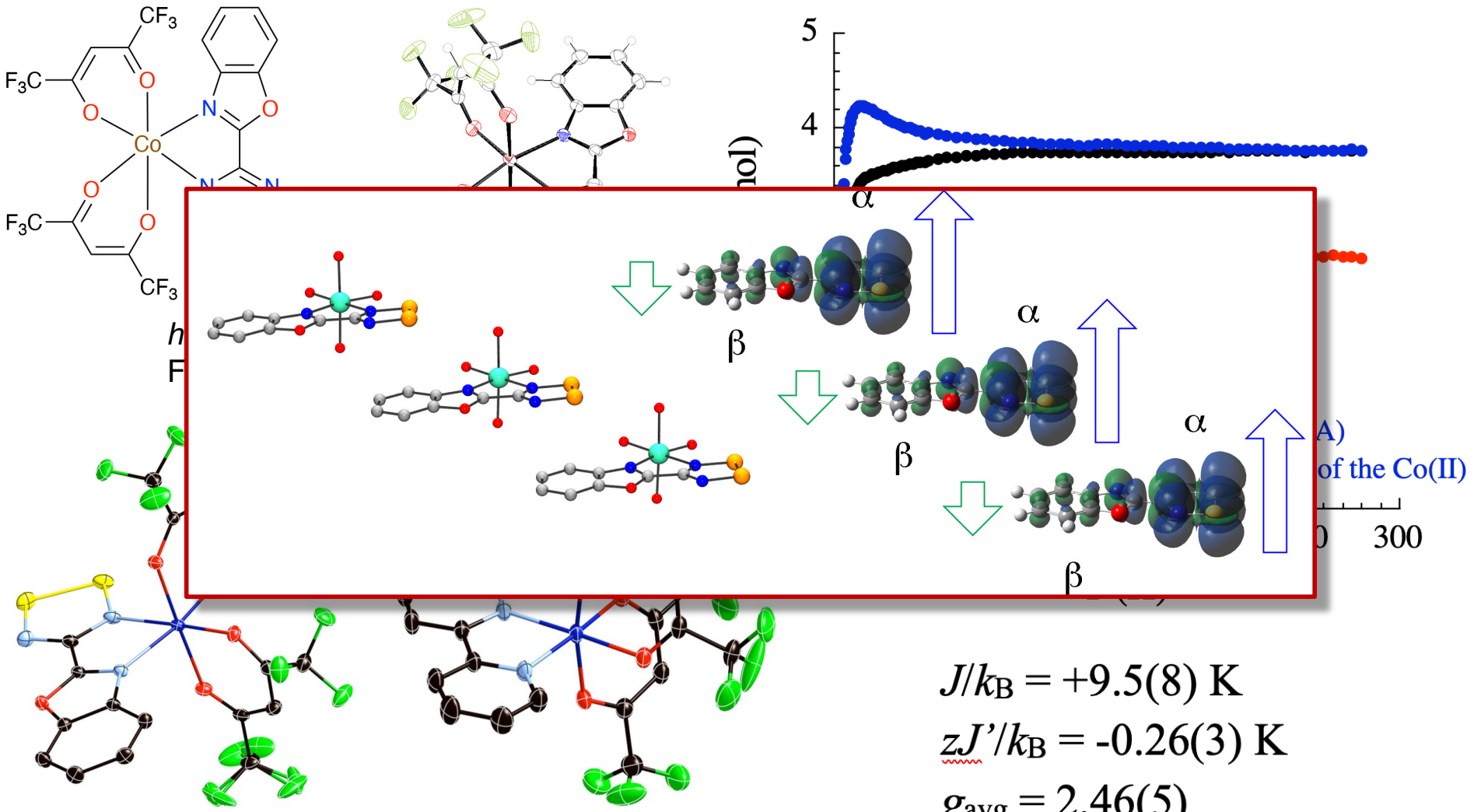
Co boaDTDA: FM Coupling



$J/k_B = +9.5(8)$ K

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$g_{avg} = 2.46(5)$

$\hat{H} = -2J\{\hat{S}_{Co} \bullet \hat{S}_{rad}\}$

$Co(hfac)_2(DTDA)$ $Co(hfac)_2(bpy)$

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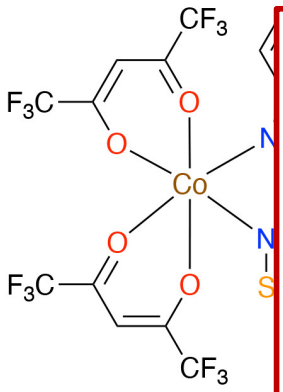
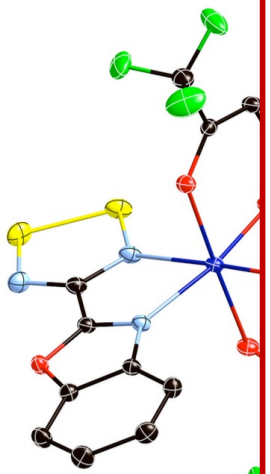
Co boaDTDA: FM Coupling

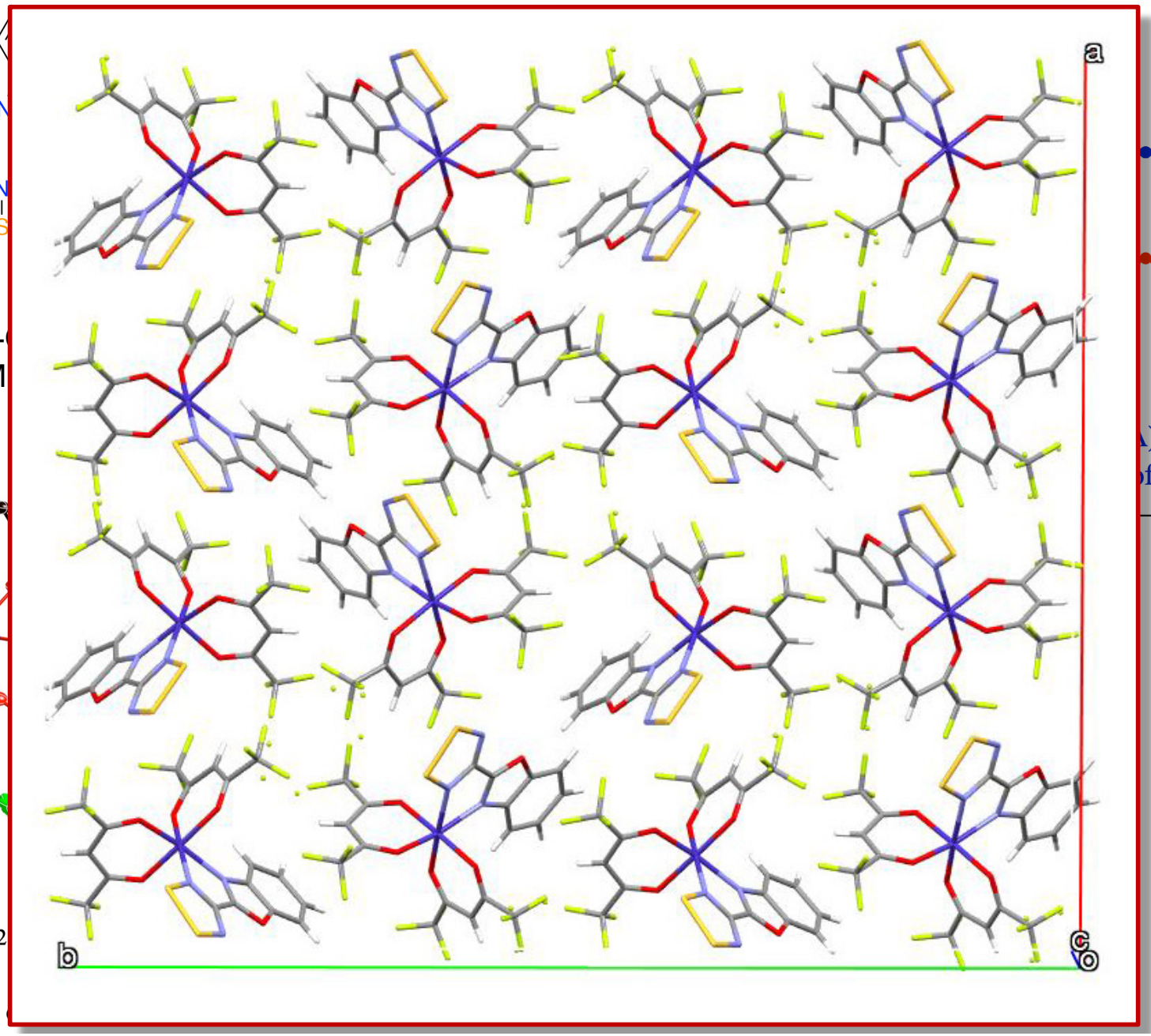


hs-

FM



Co(hfac)$_2$



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f the Co(II)

300

90

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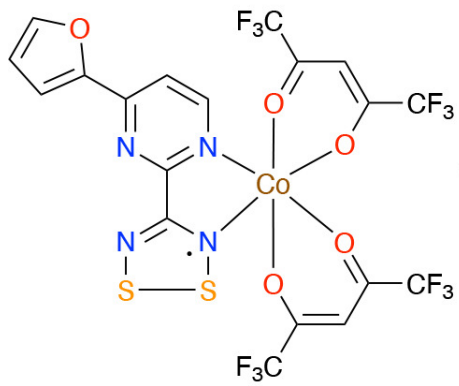
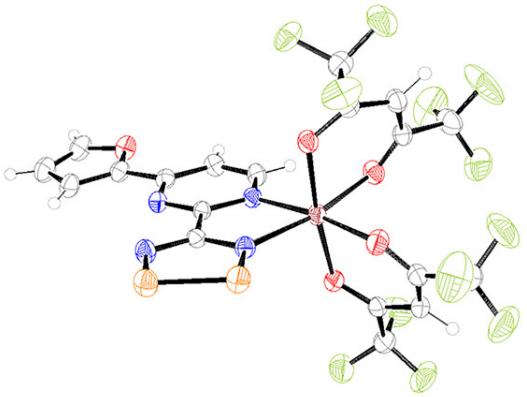
Co fpymDTDA: Ising Model & FM





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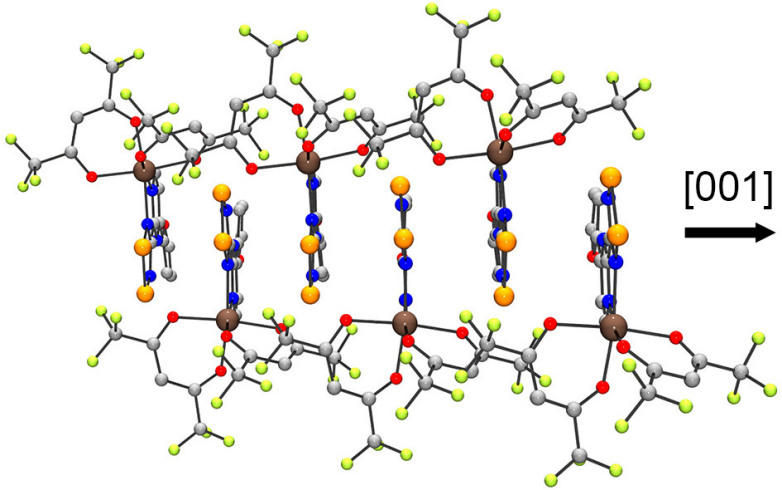

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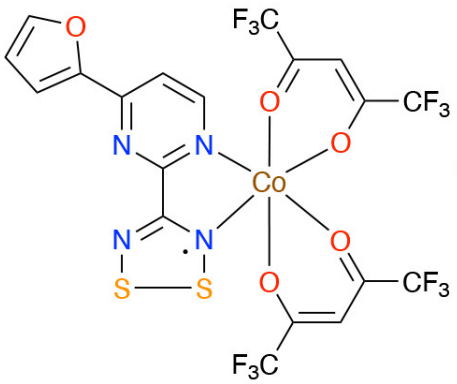
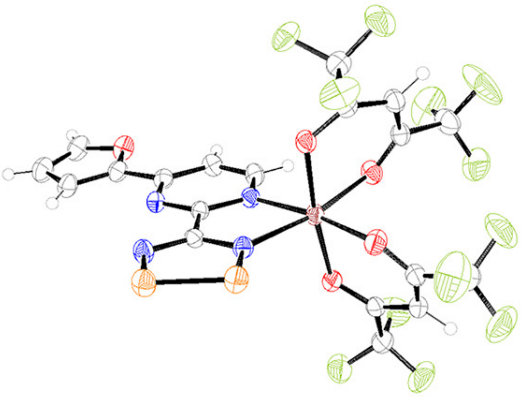
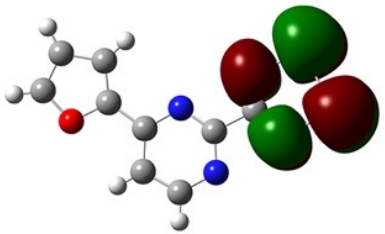
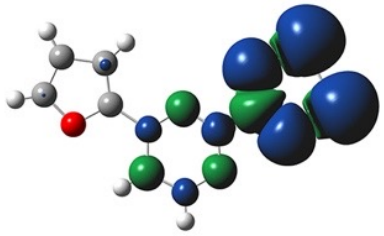


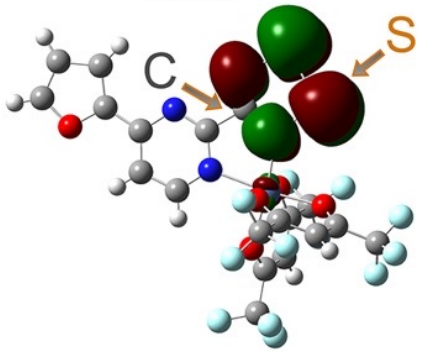


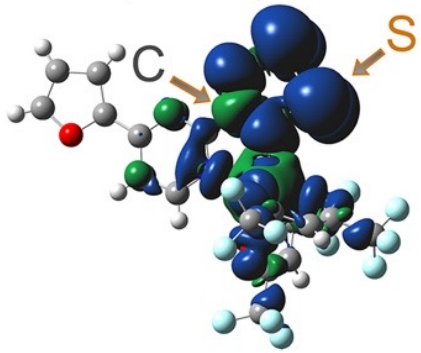




SOMO

spin density





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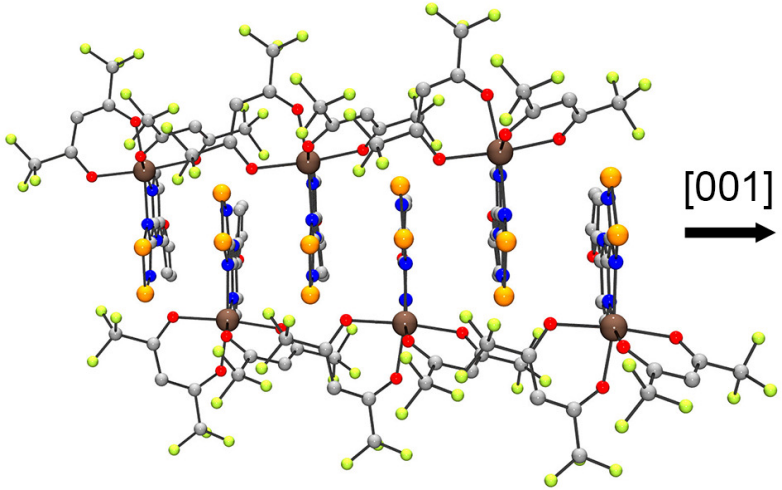
Co fpymDTDA: Ising Model & FM



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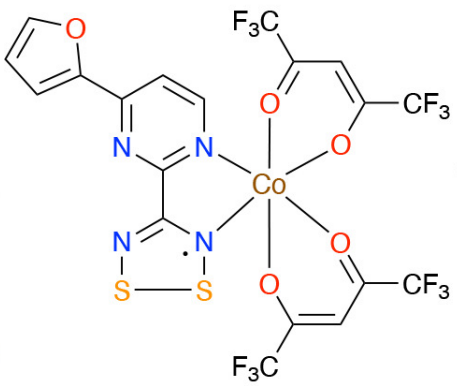
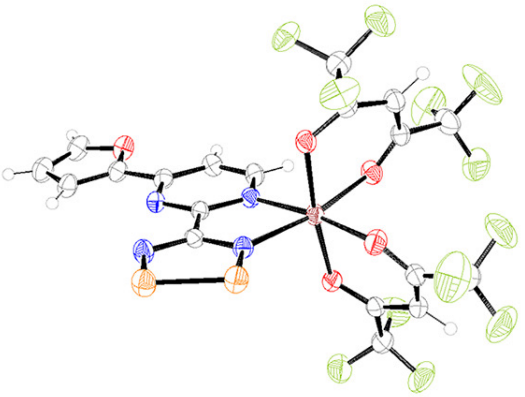
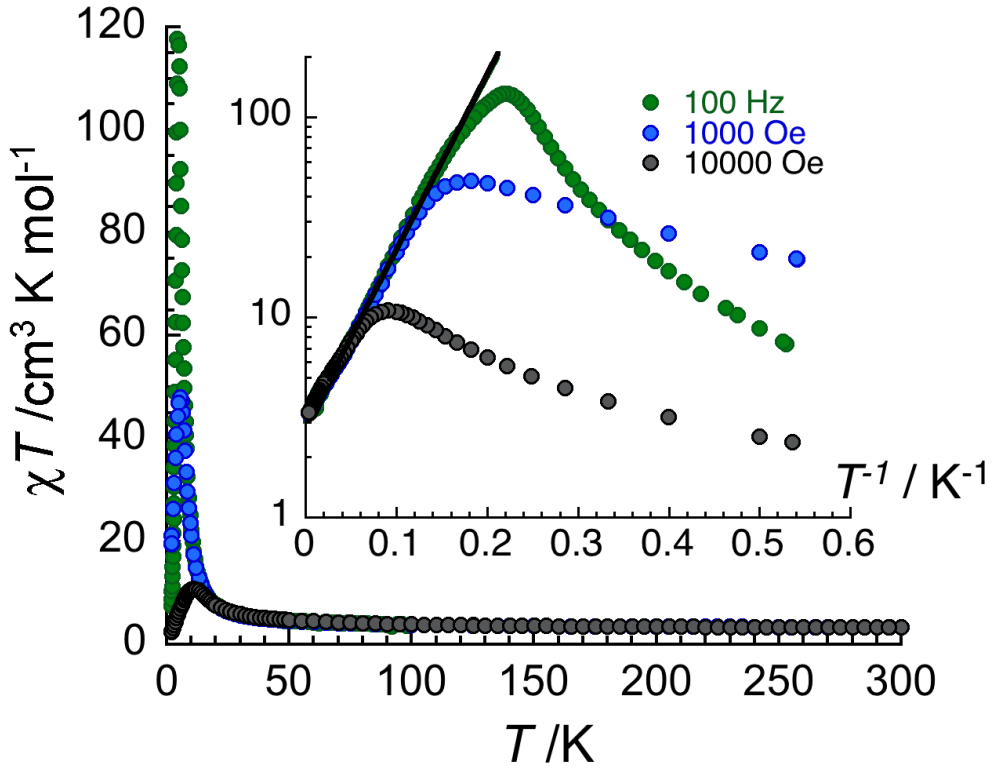
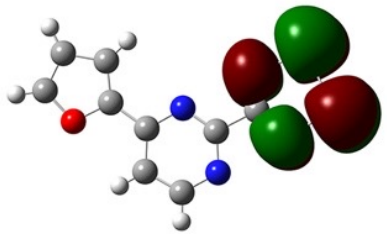


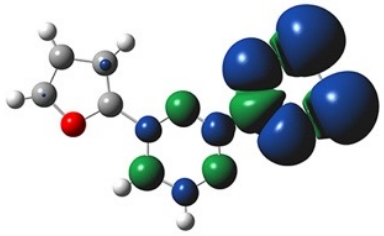


hs-Co(II) complex $S_T = 2$

FM intermolecular interactions

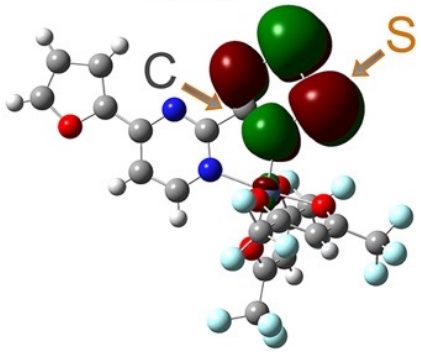


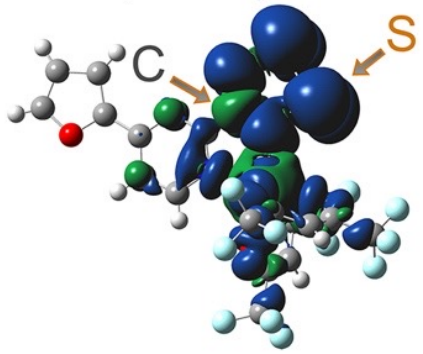




SOMO

spin density





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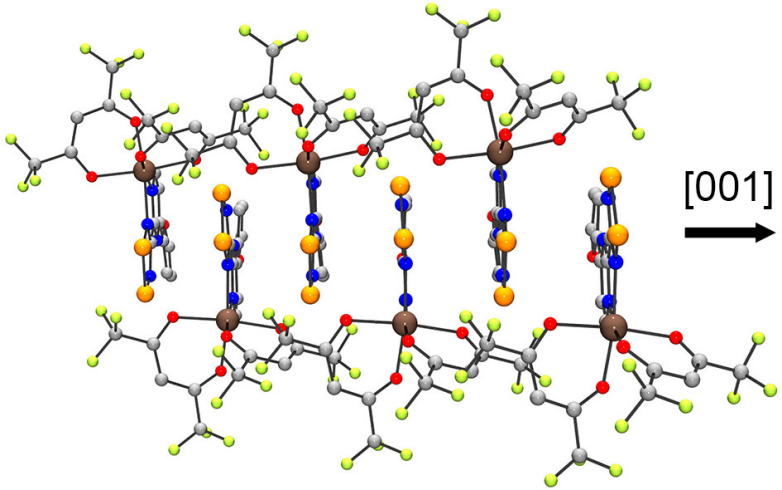
Co fpymDTDA: Ising Model & FM



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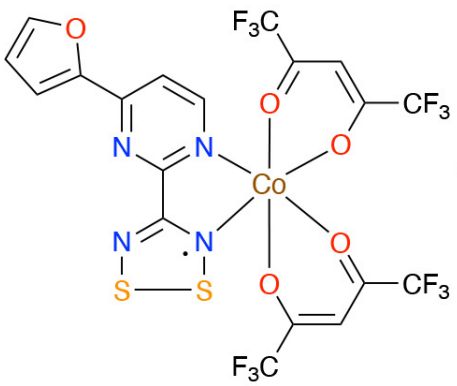
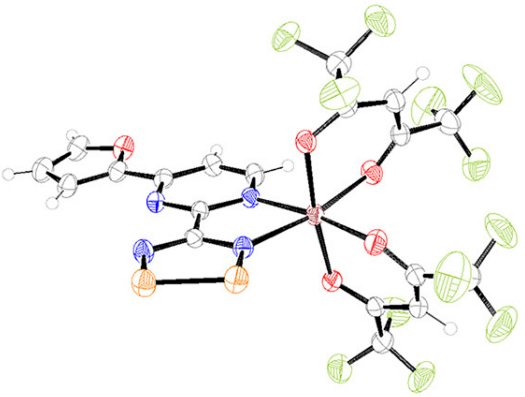
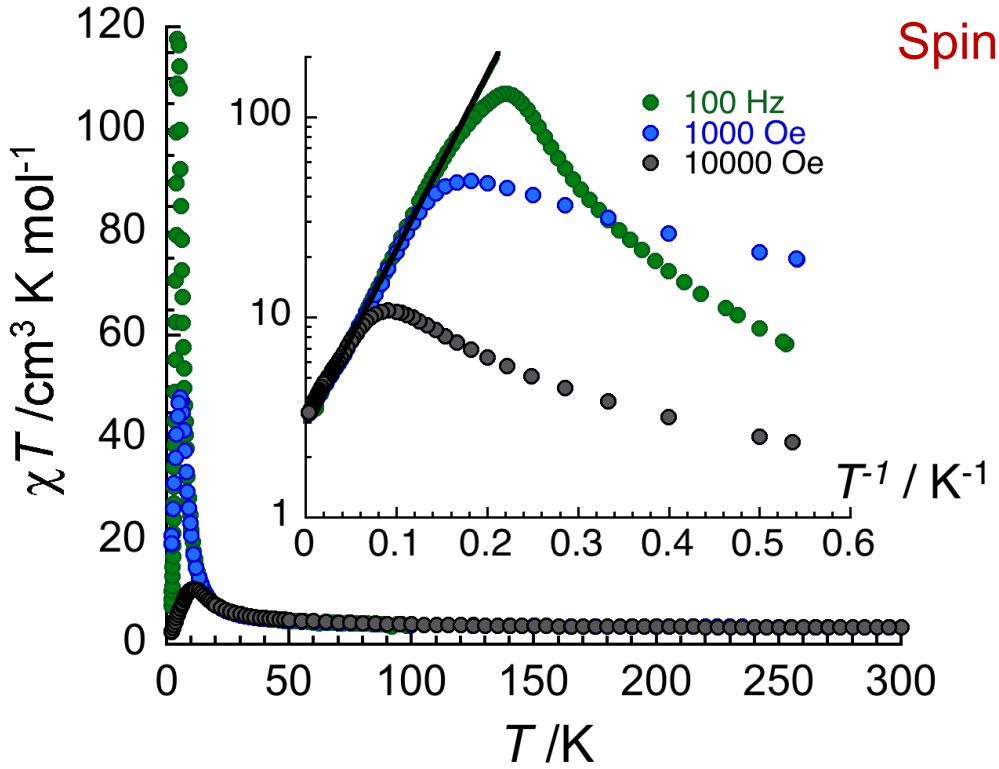




Ising-like Spin Chain

hs-Co(II) complex $S_T = 2$
FM intermolecular interactions

$$\frac{\chi T}{C} = \frac{2\xi}{l} \approx exp\left(\frac{\Delta_\xi}{k_B T}\right)$$



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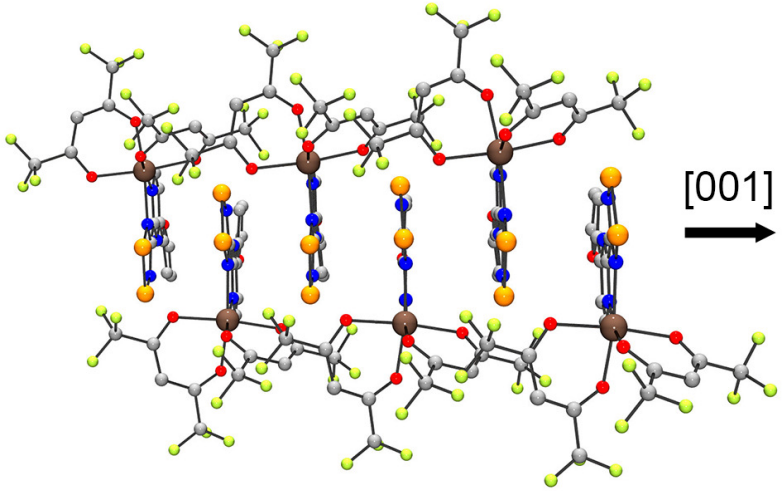
Co fpymDTDA: Ising Model & FM



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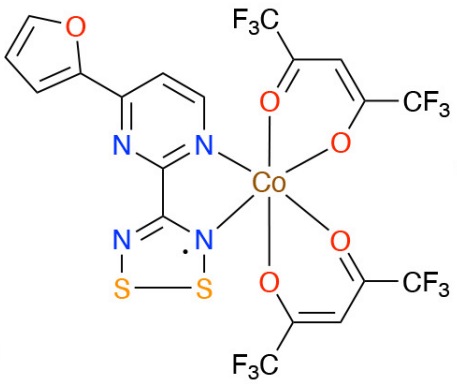

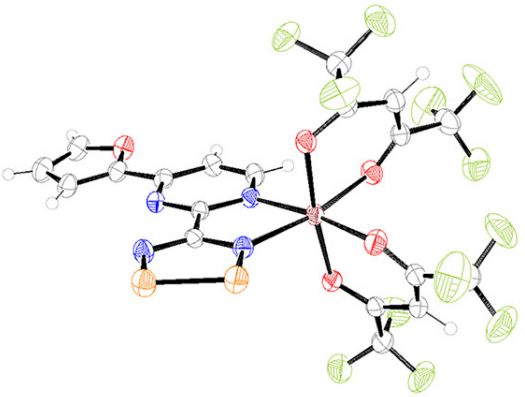

Ising-like Spin Chain

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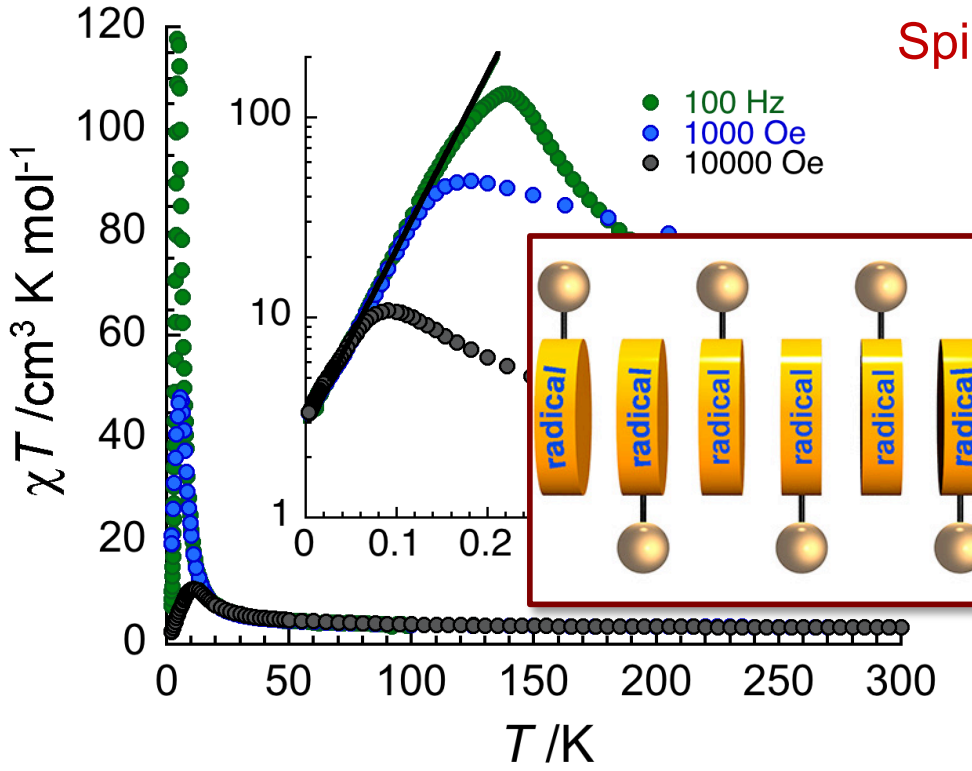

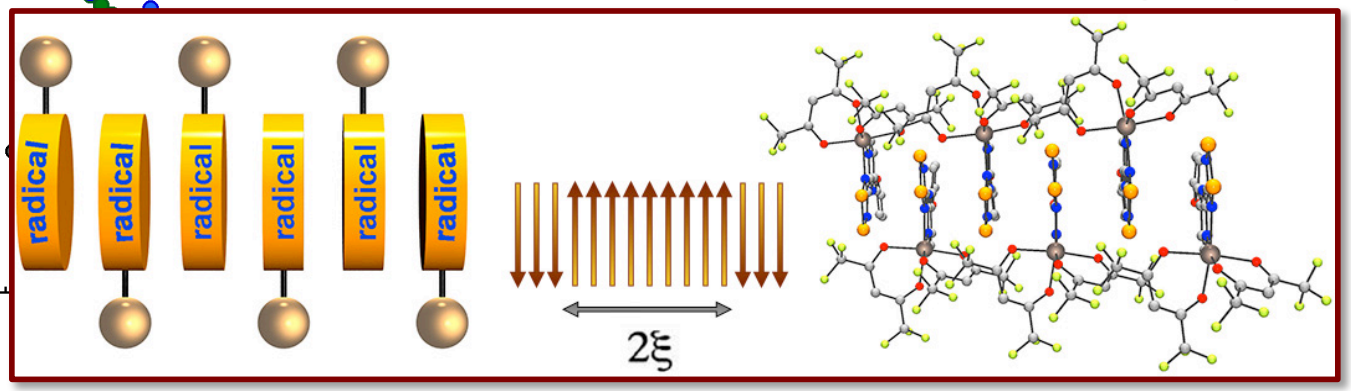

where Δ_ξ is the formation energy of a domain wall along the chain

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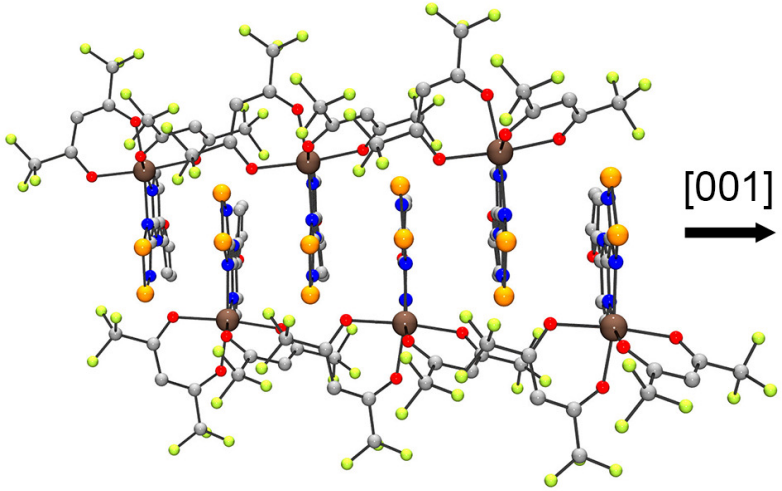
Co fpymDTDA: Ising Model & FM



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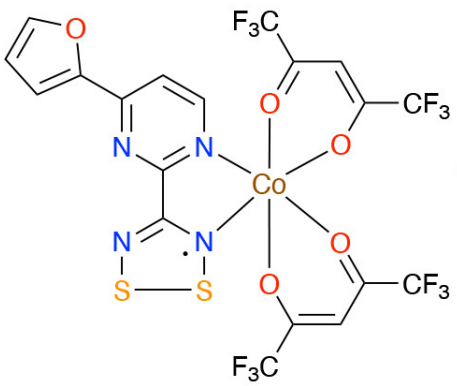
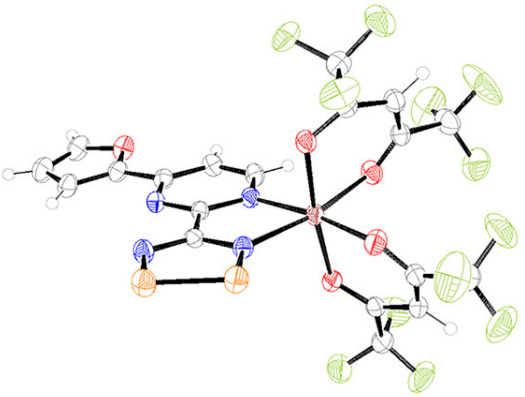
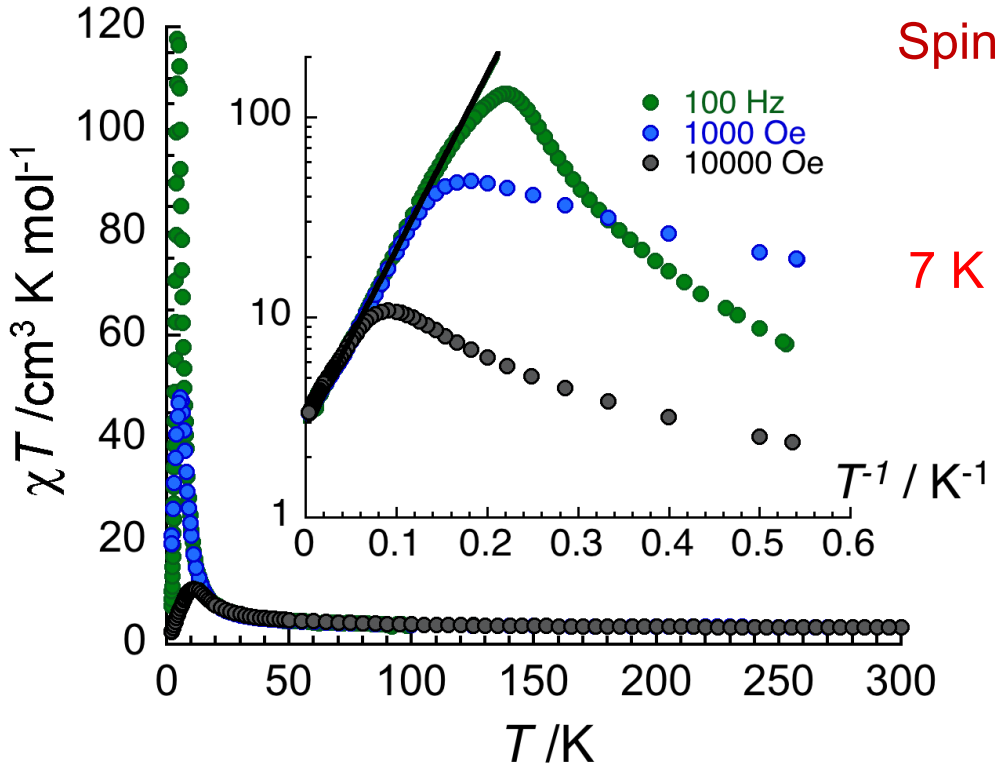




Ising-like Spin Chain

hs-Co(II) complex $S_T = 2$
FM intermolecular interactions

$$\frac{\chi T}{C} = \frac{2\xi}{l} \approx exp\left(\frac{\Delta_\xi}{k_B T}\right)$$



7 K < *T* < 30 K

$\Delta_\xi = 4J_{eff}S_T^2$
Δ_ξ/k_B can be estimated ~ 21 K
$J_{eff}/k_B = +1.3$ K

where Δ_ξ is the formation energy of a domain wall along the chain

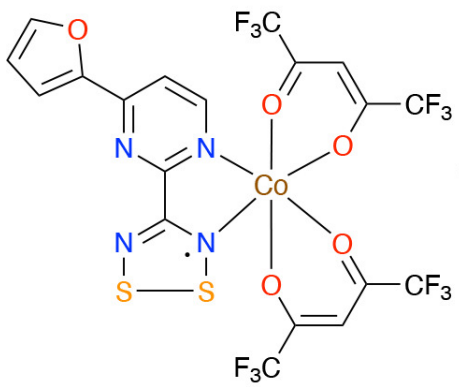
Maahs, A. C.; Borg, G. C; Ghazzali, M.; Soldatov, D. V.; Rouzières, M.; Clérac, R.; Preuss, K. E. *Chem. Eur. J.* **2024**, *30*, e202403220.

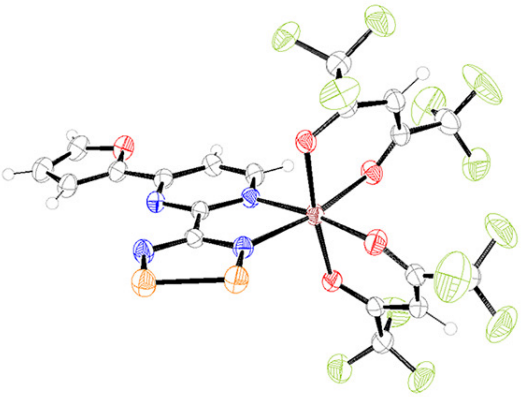
Co fpymDTDA: Ising Model & FM

$g_{avg} = 2.54$

$T_C = 4.6$ K

FM Ordering





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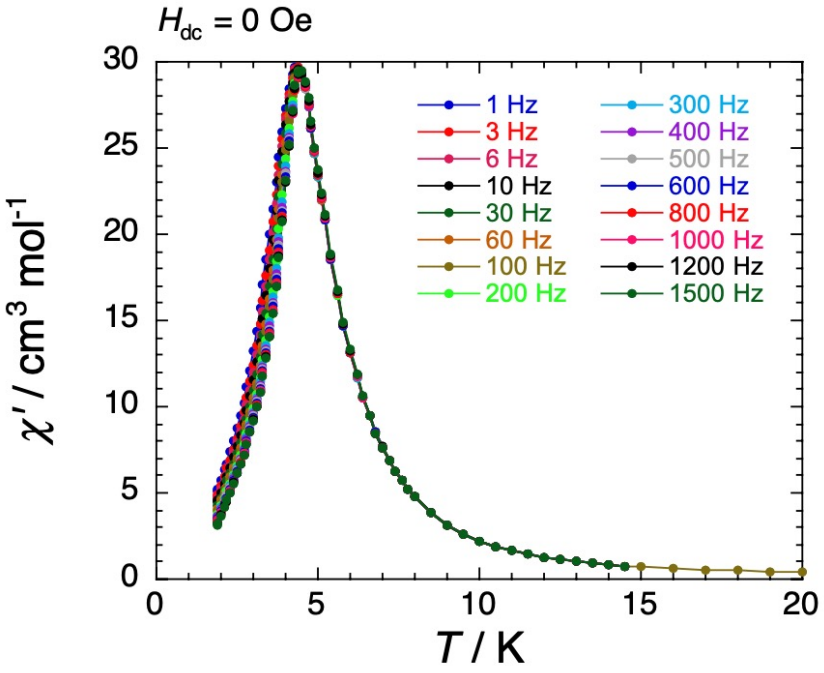

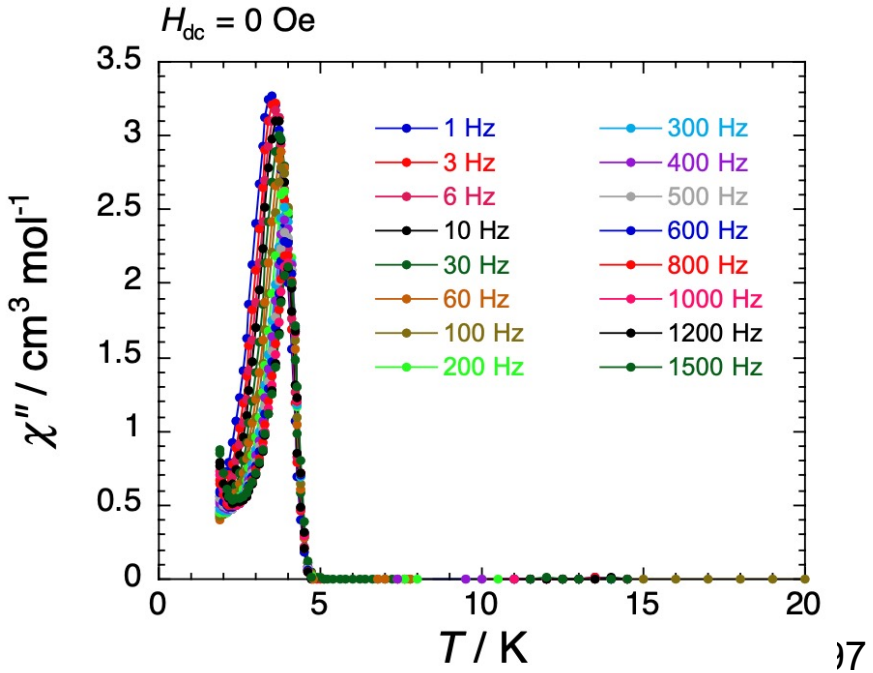

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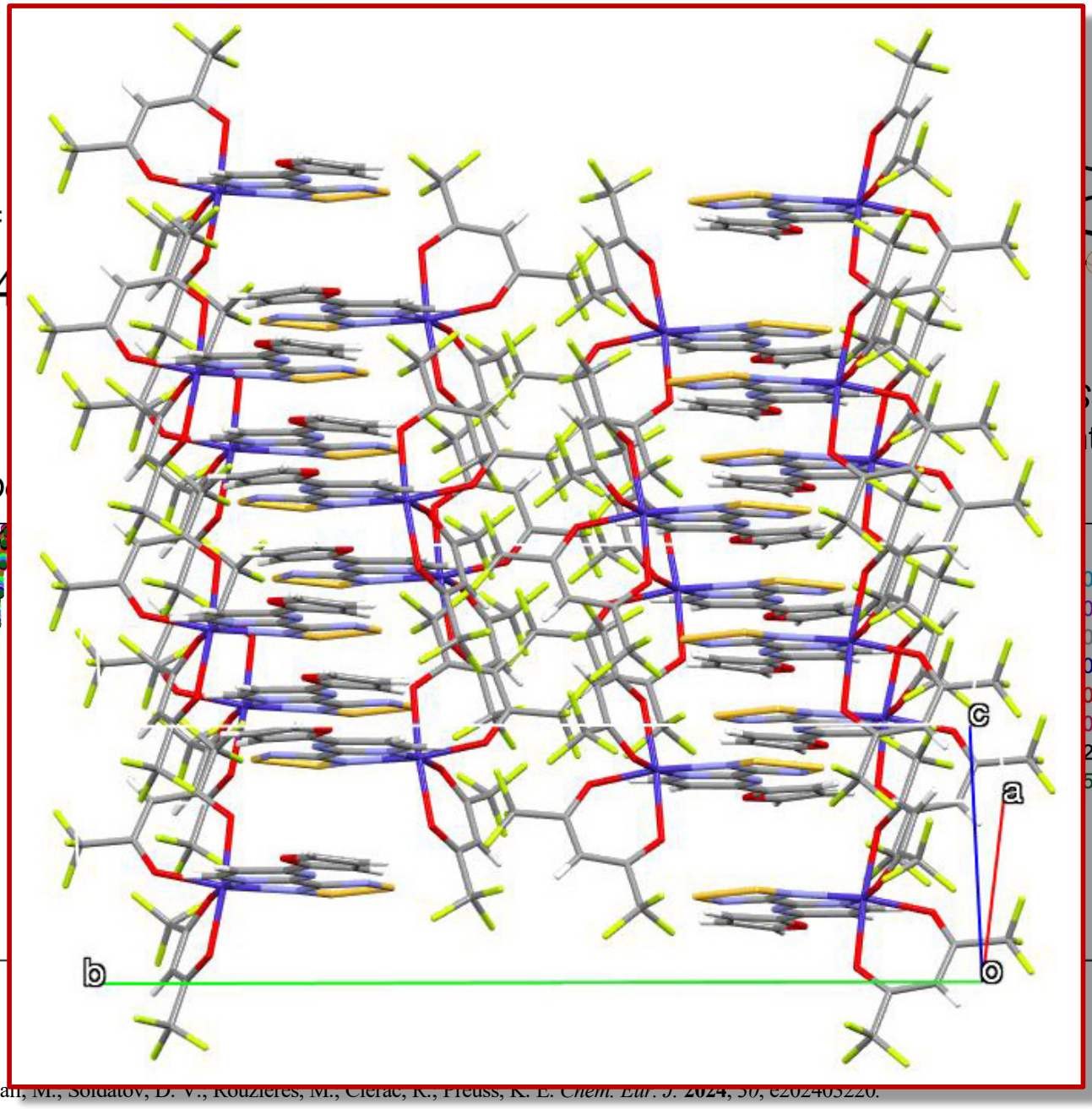
Co fpymDTDA: Ising Model & FM

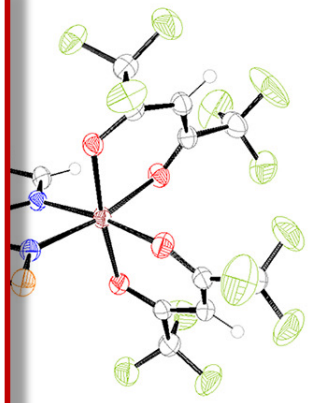
g_{avg} =

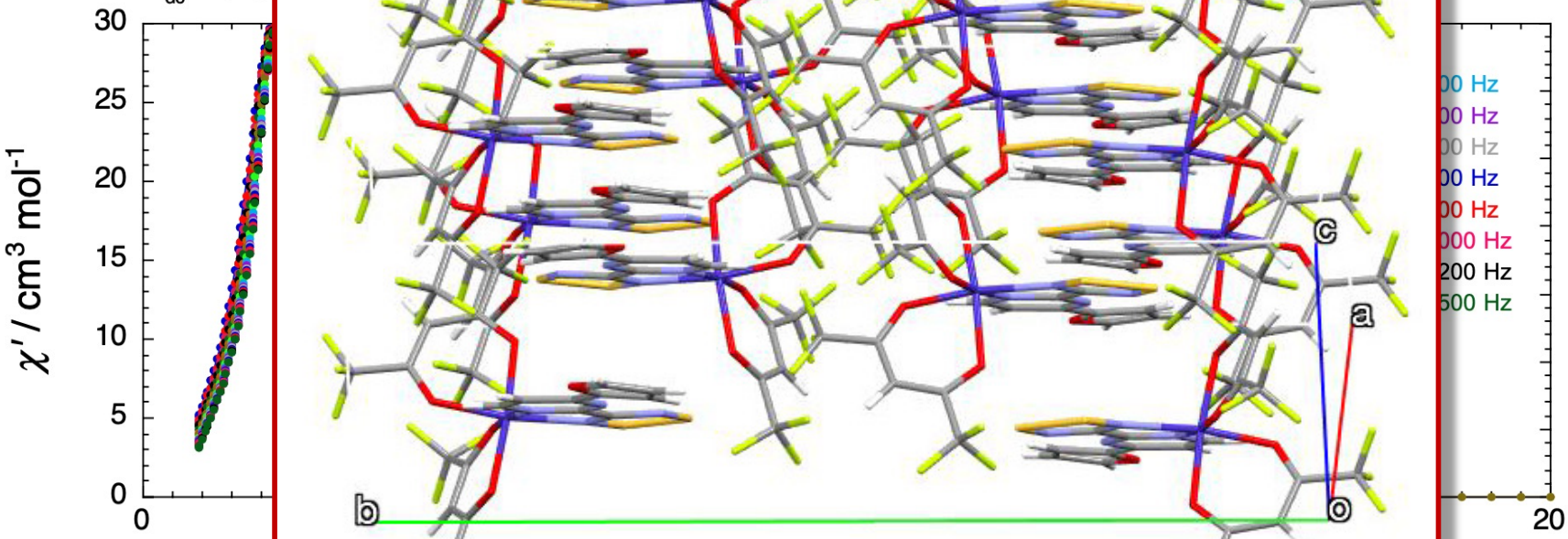
T_C = 4

S_T = 2

teractions







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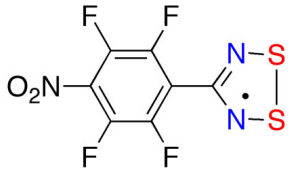
Maahs, A. C.; Borg, G. C; Ghazzali, M.; Soldatov, D. V.; Rouzières, M.; Clérac, R.; Preuss, K. E. *Chem. Eur. J.* **2024**, 30, e202403220.

Thiazyl Radicals - Properties



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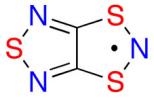
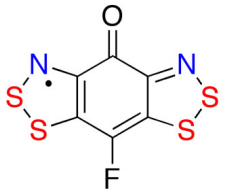


RT magnetic bistability

W. Fujita & K. Awaga,
Science, **1999**, *286*, 261.



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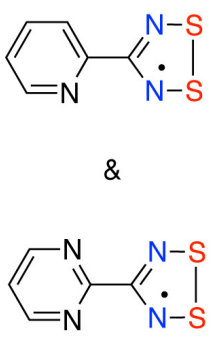

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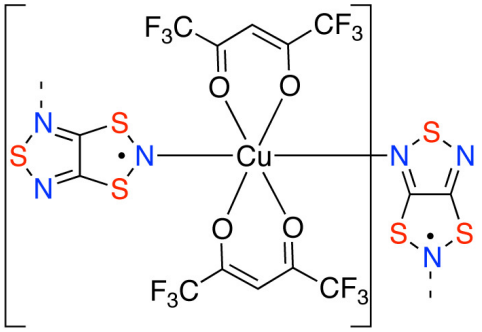

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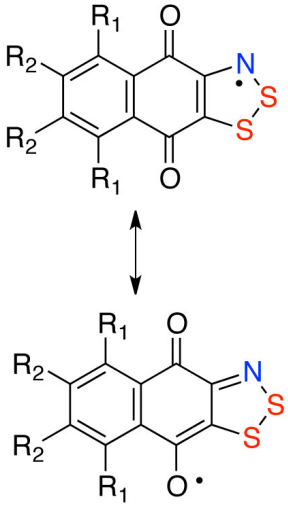

Preuss, *et al.*, *Chem. Commun.* **2012**, *46*, 10963.
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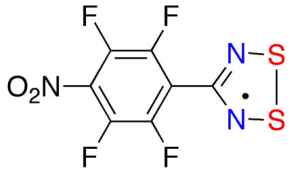
Thiazyl Radicals - Properties



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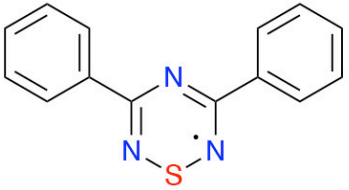

3 stable oxidation states

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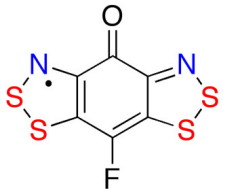

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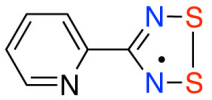

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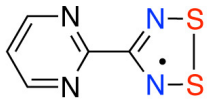

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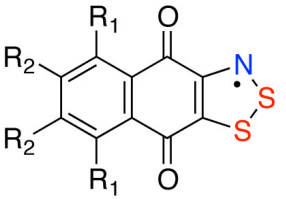

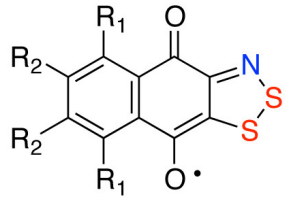

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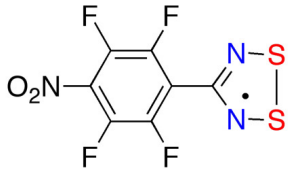

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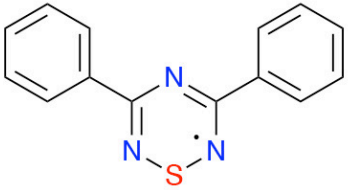

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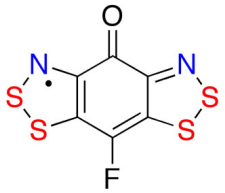

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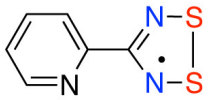

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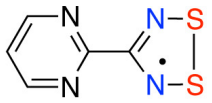

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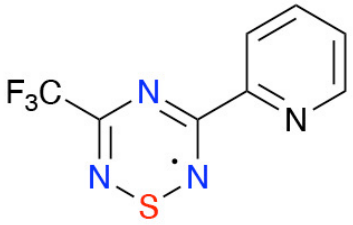
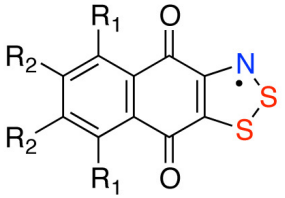
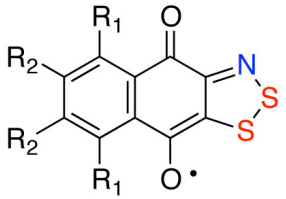


Boeré & Preuss, *et al.* unpublished work





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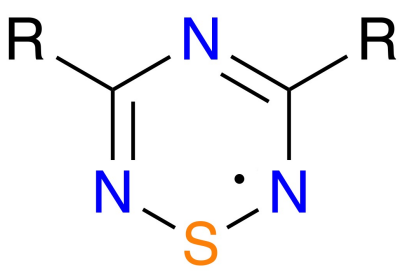
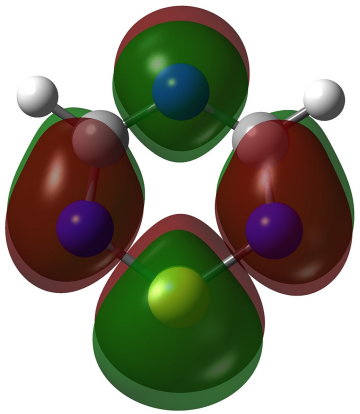
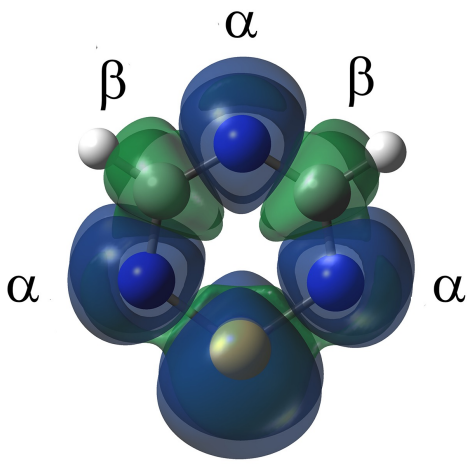
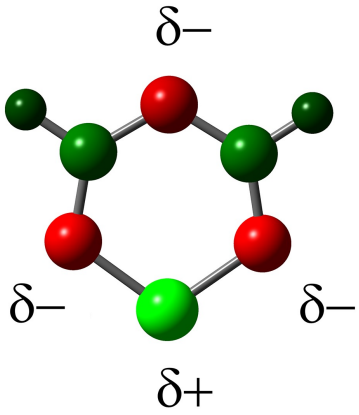
1,2,4,6-Thiatriazinyl Radical

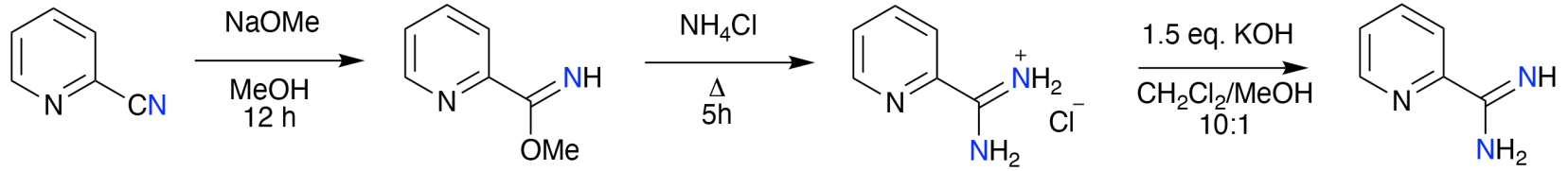
1,2,4,6-Thiatriazinyl **Neutral Radical**

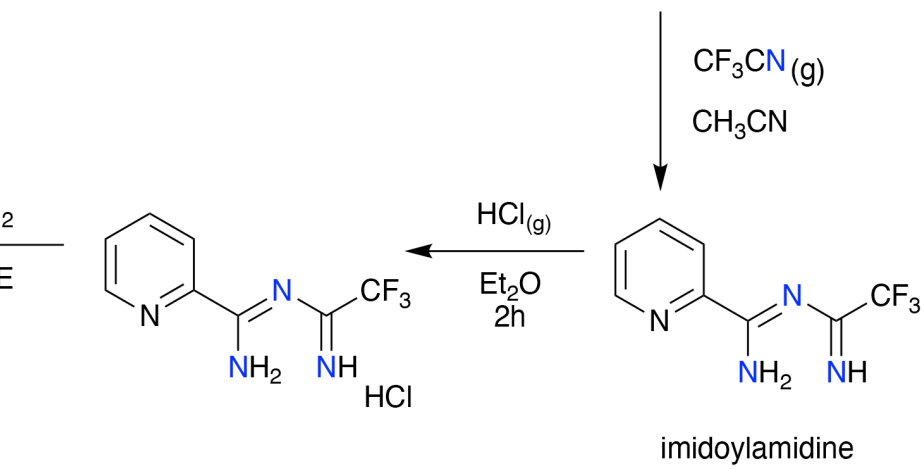












Ibrahim. Boeré. & Preuss. *unpublished*

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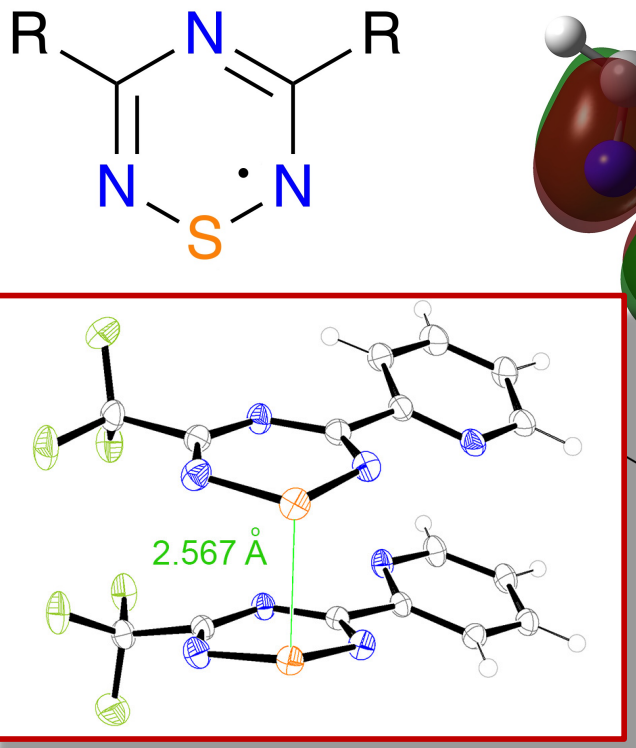

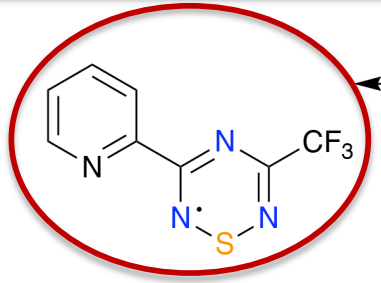

0.5 $SbPh_3$

CH_3CN

1h

SCl_2

DCE

6h

$HCl_{(g)}$

Et_2O

2h

HCl

imidoylamidine

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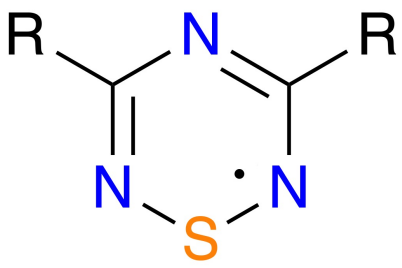
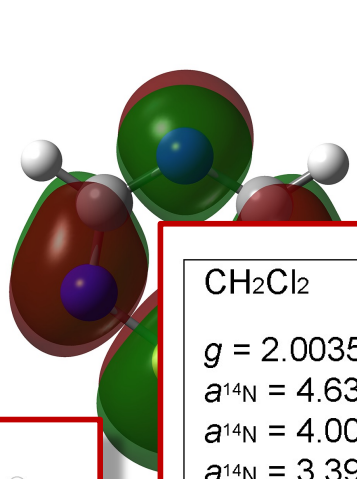
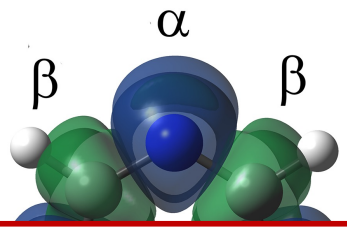
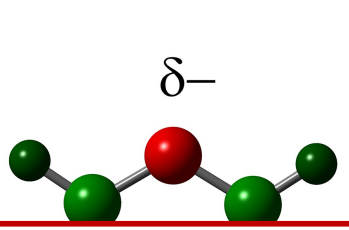
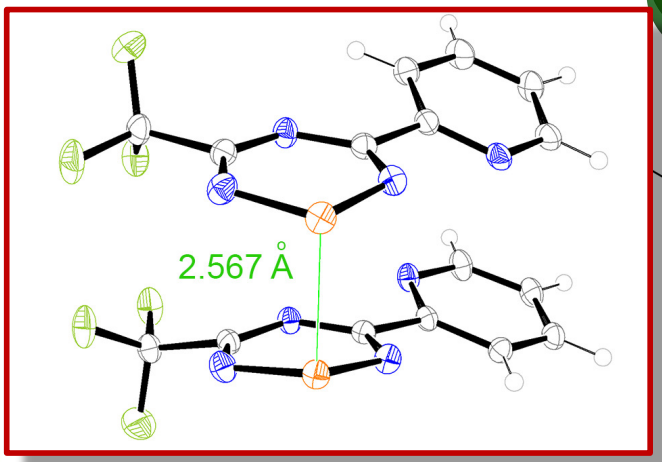
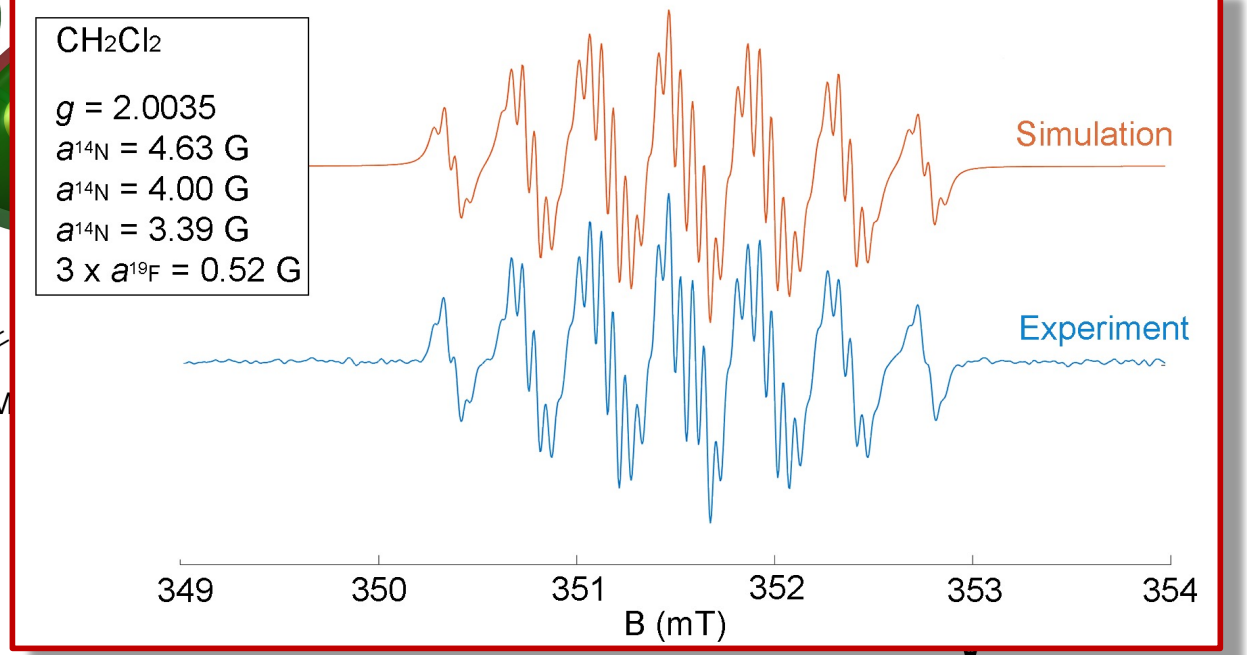


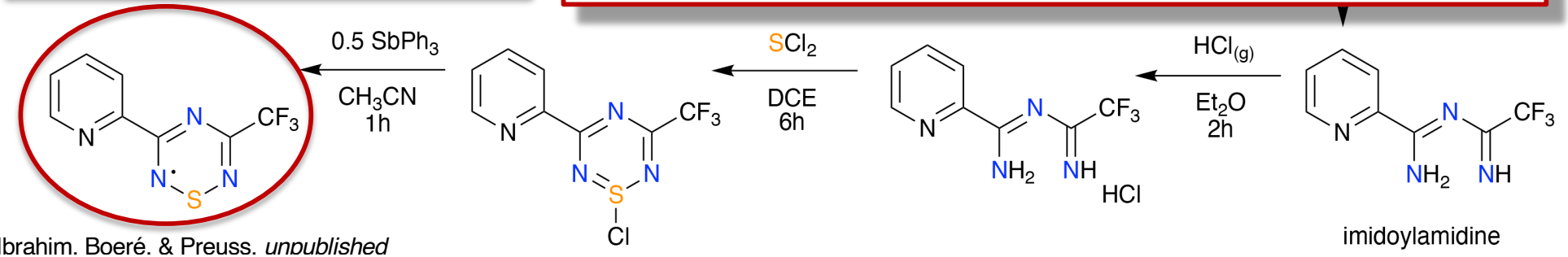






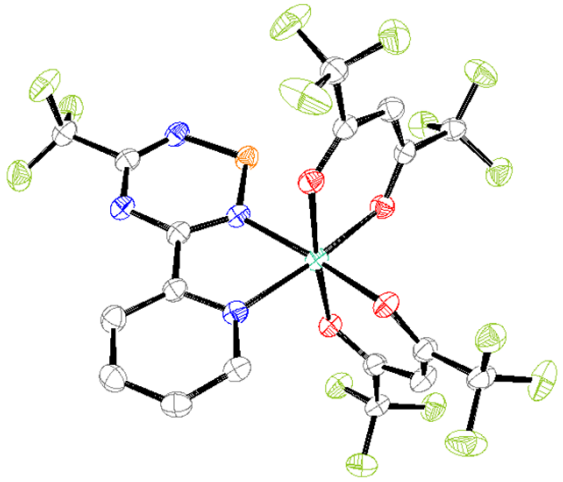






Ibrahim. Boeré. & Preuss. *unpublished*

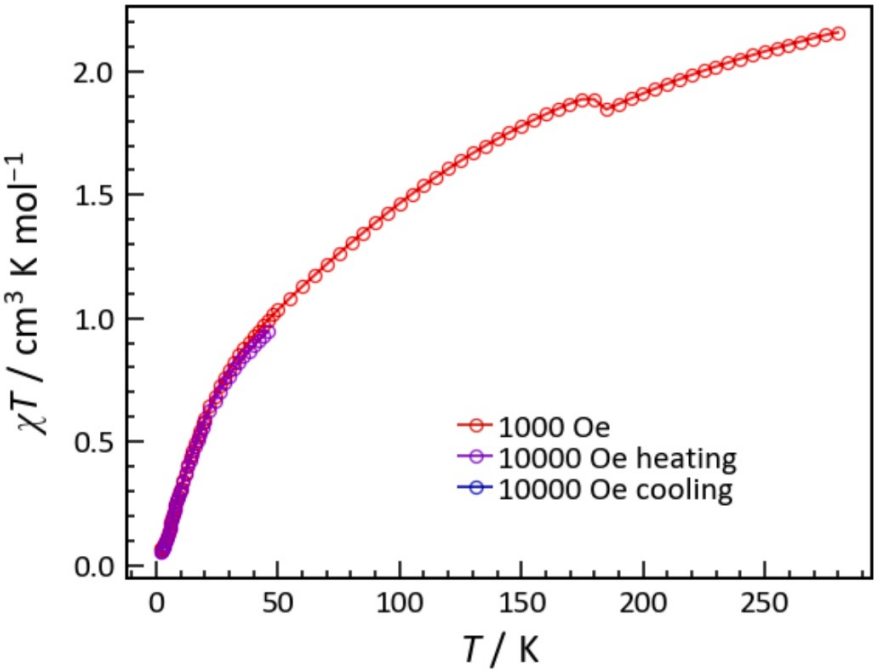
CF_3pyTTA Tm complexes



Ni complex

Awful data
Very dirty

What is that kink @~180 K ??



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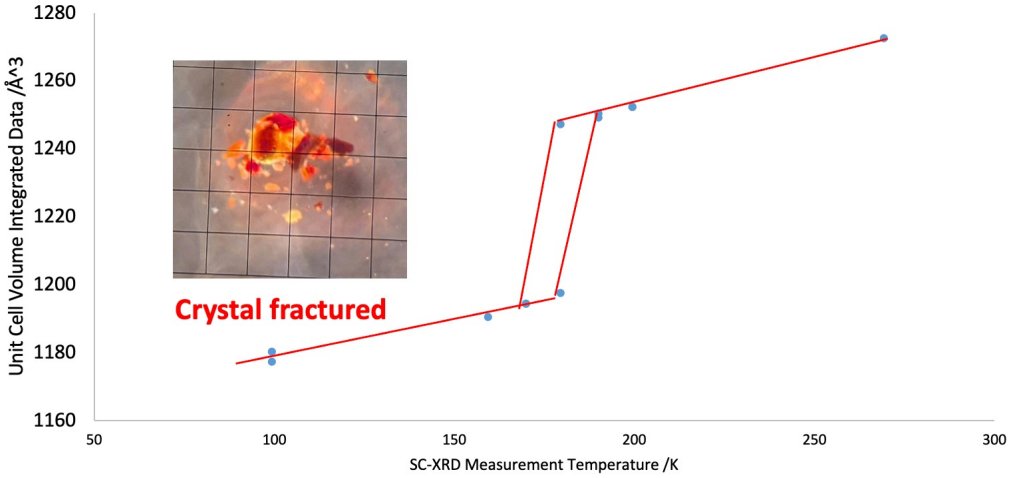

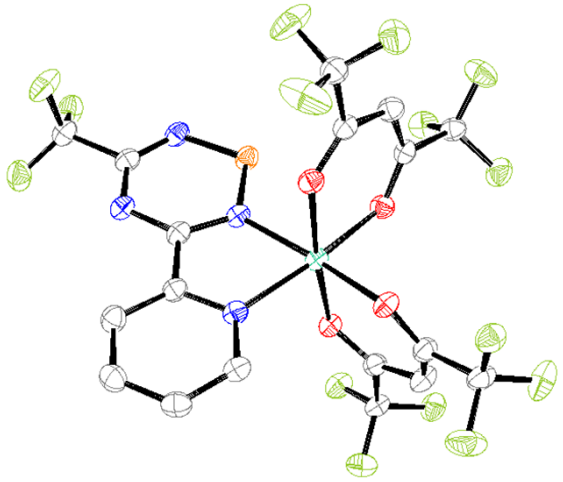

Ni complex

Cell volume vs T plot of $Ni(hfac)_2PyCF_3TTA$

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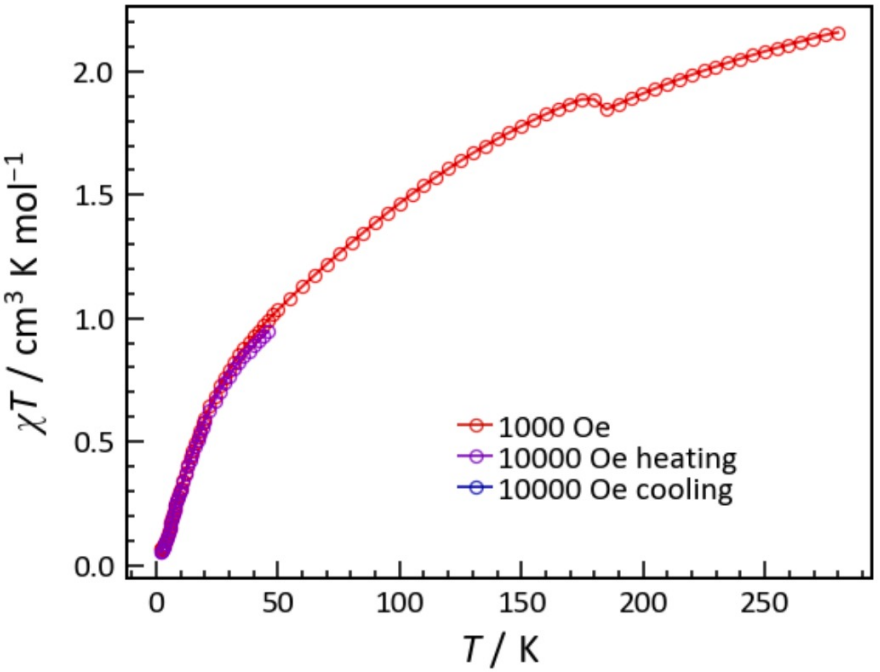
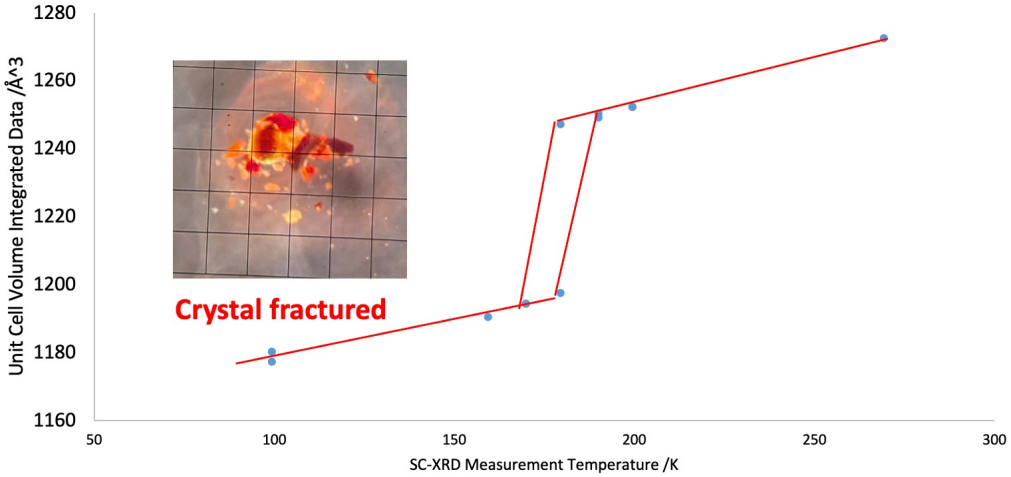
Very dirty

What is that kink @~180 K ??

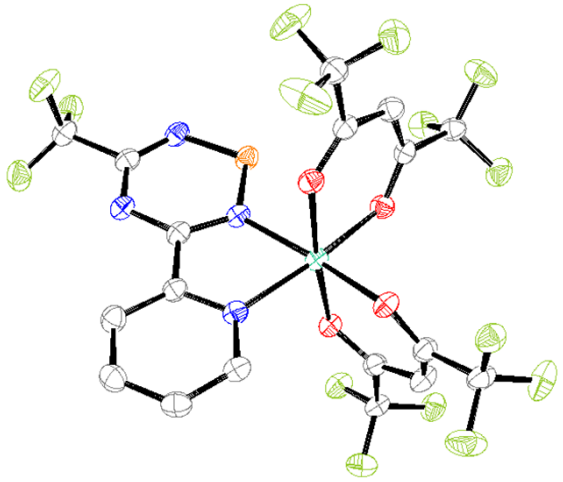


Ibrahim, Boeré, & Preuss, *unpublished*

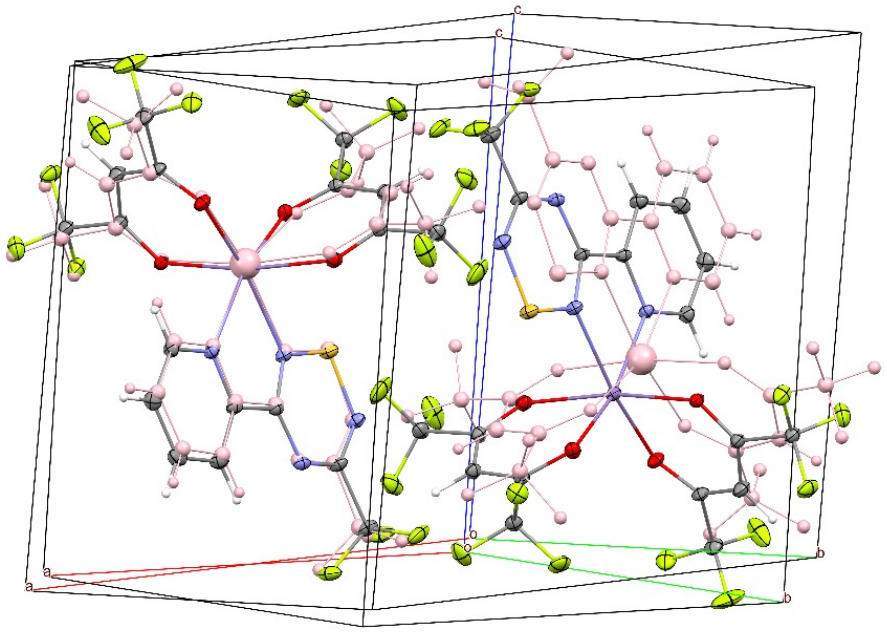
CF_3pyTTA Tm complexes



Cell volume vs T plot of Ni(hfac)$_2$PyCF$_3$TTA



Ni complex



Mn complex
unit cell
T above/below transition

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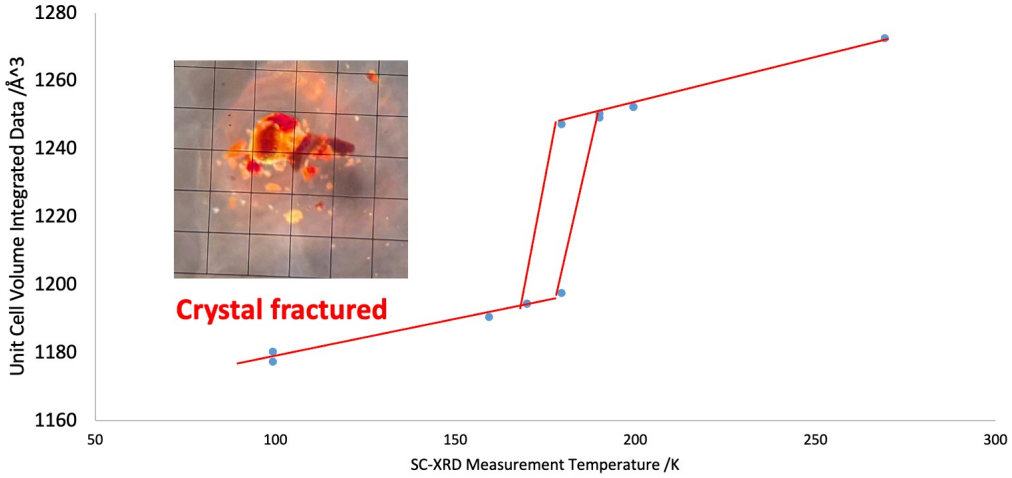
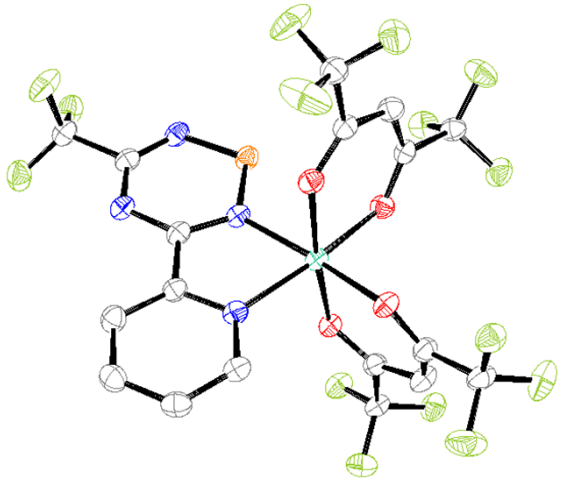
CF_3pyTTA Tm complexes



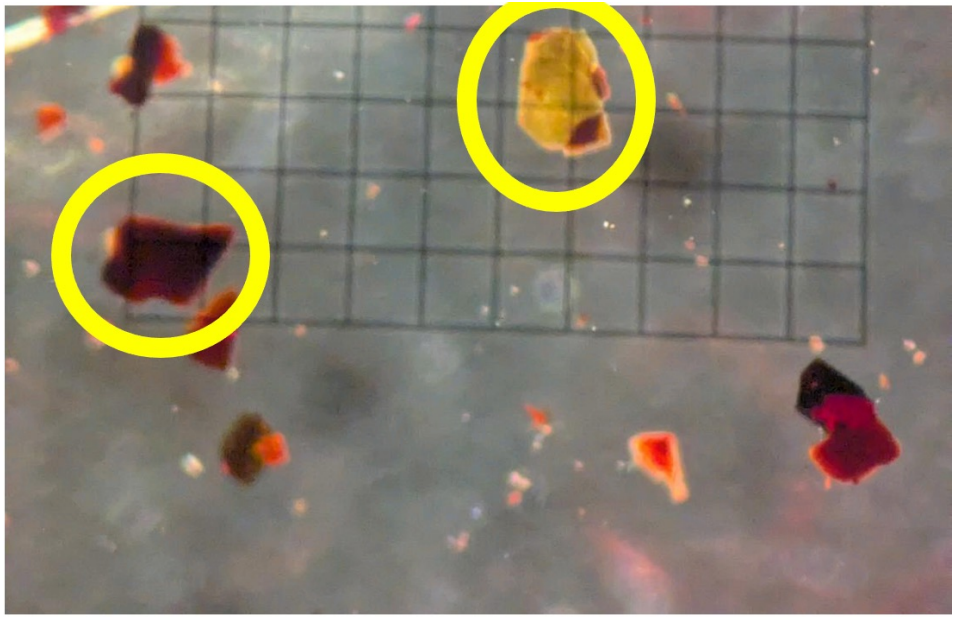
Cell volume vs T plot of Ni(hfac)$_2$PyCF$_3$TTA



Ni complex

No, this is *not* dirty!

This is dichroism!



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Take Home Message