# Variation in Electronic Properties in Novel Single-Component Organic Solids

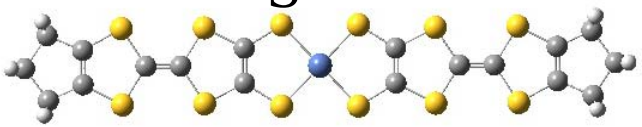
S. Ishibashi[1)] and K. Terakura[2)]

[1)] RICS, AIST

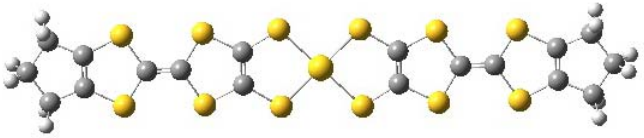
[2)] JAIST

# Molecular structures for single-component molecular solids

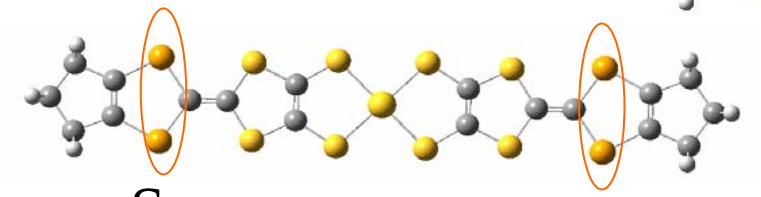
S



$Ni(tmdt)_2$

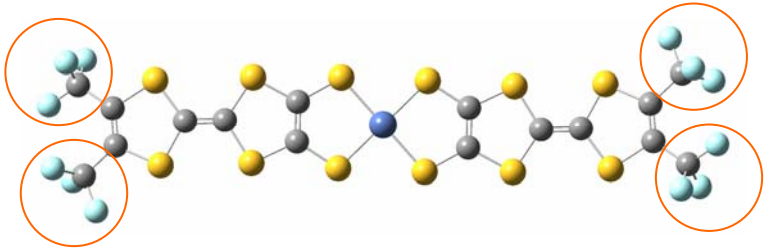


$Au(tmdt)_2$



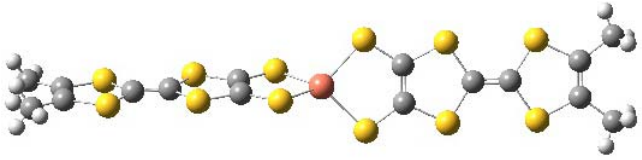
Se

$Au(tmstfdt)_2$

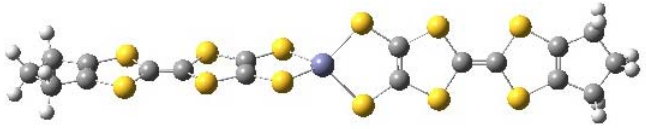


$-CF_3$

$Ni(hfdt)_2$



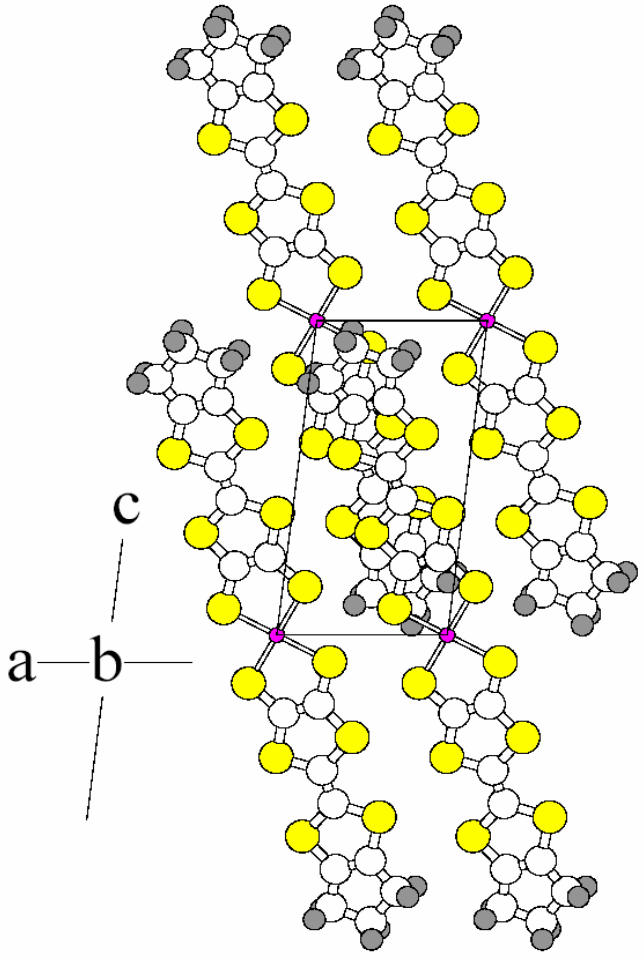
$Cu(dmdt)_2$

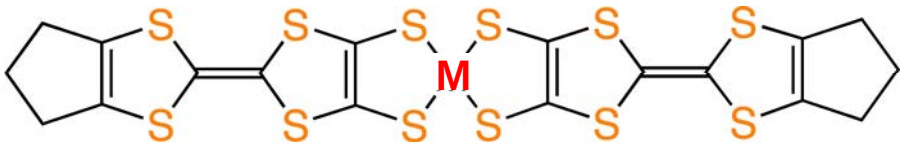


$Zn(tmdt)_2$

# Single-component conducting organic solids

**Neighboring molecules in the *a*+*c* direction overlap along *b*.**




[**M**(tmdt)$_2$]

**M**=Ni (2001)
Au (2003)

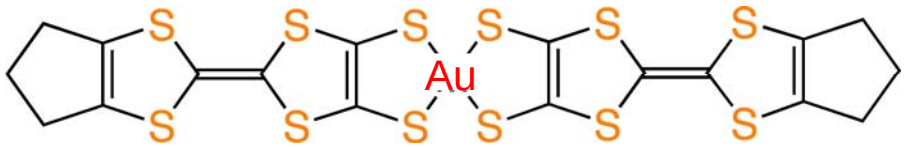
Space group P-1

Ni(tmdt)$_2$ : H. Tanaka *et al.*, Science **291**, 285 (2001).
$a$ = 6.376 Å, $b$ = 7.359 Å, $c$ = 12.012 Å
$\alpha$ = 90.384 ° , $\beta$ = 96.688 ° , $\gamma$ = 103.587 °
$V$ = 543.7 Å$^3$

Au(tmdt)$_2$ : W. Suzuki *et al.*, JACS **125**, 1486 (2003).
$a$ = 6.413 Å, $b$ = 7.551 Å, $c$ = 12.154 Å
$\alpha$ = 90.473 ° , $\beta$ = 96.698 ° , $\gamma$ = 103.008 °
$V$ = 569.2 Å$^3$

## Crystal structure of Ni(tmdt)$_2$ and Au(tmdt)$_2$

# Physical Properties of [Au(tmdt)$_2$]




[Au(tmdt)$_2$]

***ESR***

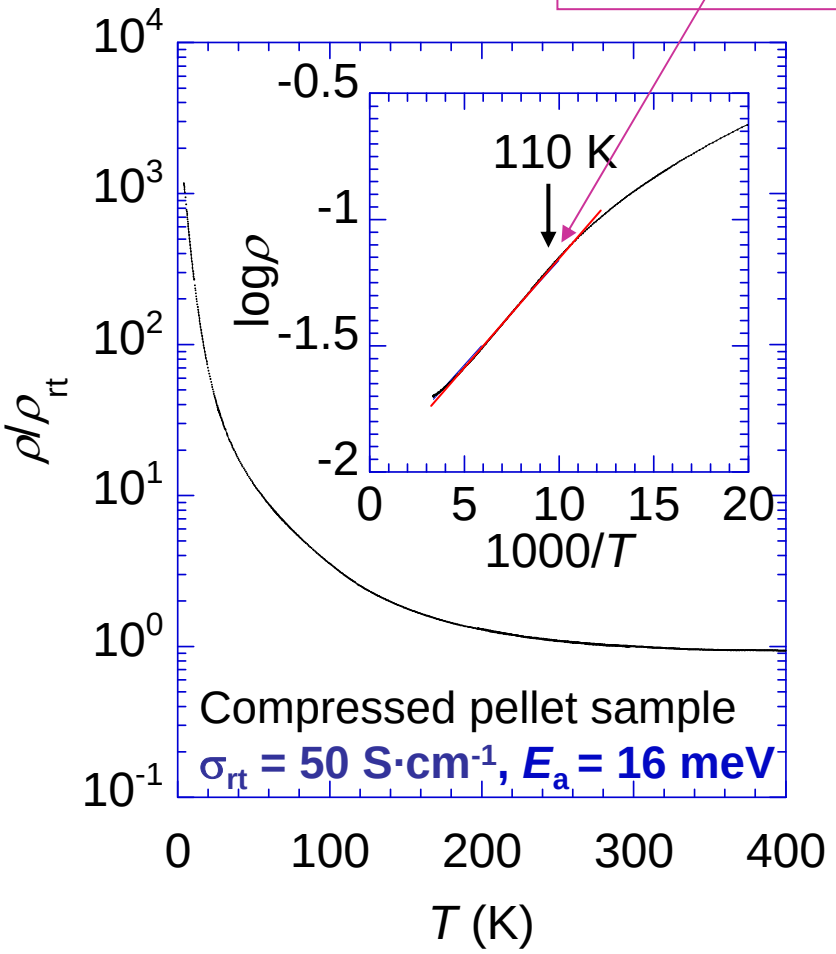
$\chi_{spin\ rt}$ = 3.8 x $10^{-4}$ emu·mol$^{-1}$

$g$ = 2.005

$\Delta H_{PP}$ = 250 G

***Conductivity***

**no anomaly!**

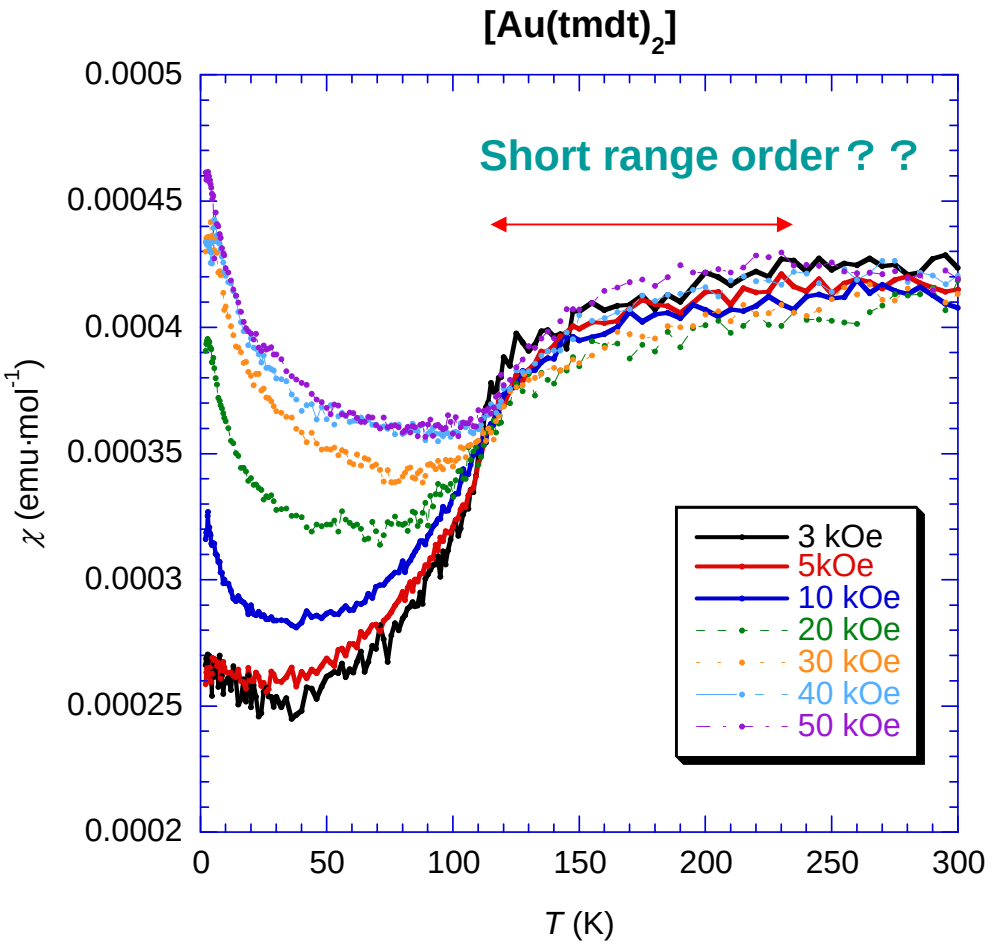



***$^1$H-NMR*** K.Miyagawa, K.Kanoda

小林ら

# Magnetic susceptibility of Au(tmdt)2 New data

**SQUID**




小林ら

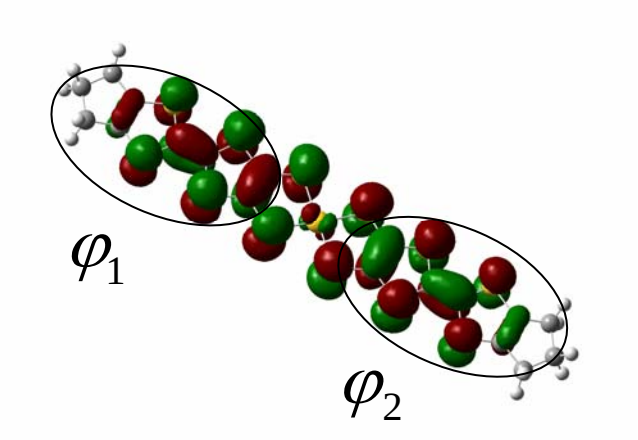
**magnetic moment: 0.3 $\mu_B$**

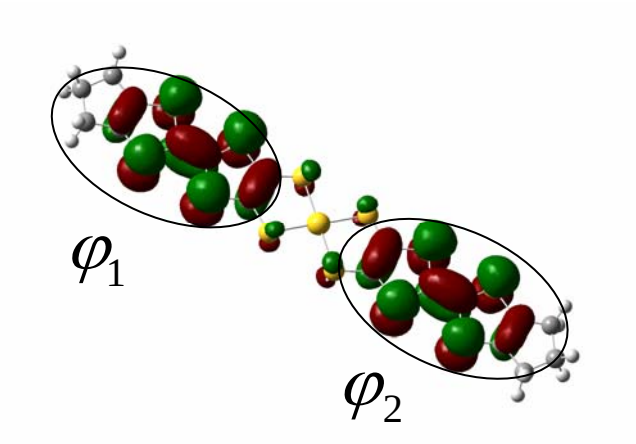
# questions to be answered

- reason for metallicity for Ni- & Au- $(tmdt)_2$
- AF configuration of $Au(tmdt)_2$
- reason for high $T_N$ for $Au(tmdt)_2$
- reason for weak anomaly in resistivity at $T_N$
- effects of substitution in ligand
- different molecular conformation

  $Au(tmdt)_2$ is planar while $Cu(dmdt)_2$ is twisted.
- why no magnetic long-range order for $Cu(dmdt)_2$ despite the presence of localized moment on Cu?

# Two important molecular orbitals near Fermi level




$$\phi_- \propto \varphi_1 - \varphi_2$$

$$\phi_+ \propto \varphi_1 + \varphi_2$$

**LUMO for Ni(tmdt)$_2$**

**HOMO for Ni(tmdt)$_2$**

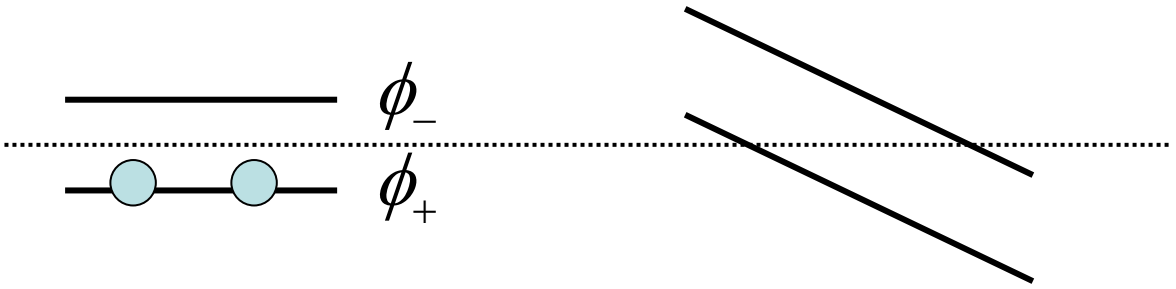
**SOMO for Au(tmdt)$_2$**

**HOMO-1 for Au(tmdt)$_2$**

$\varepsilon_- - \varepsilon_+ = 0.36$ eV : for isolated molecule of Ni(tmdt)$_2$

C. Rovira et al., Phys. Rev. B 65, 81104 (2002)

=0.16 eV: for isolated molecule of Au(tmdt)$_2$

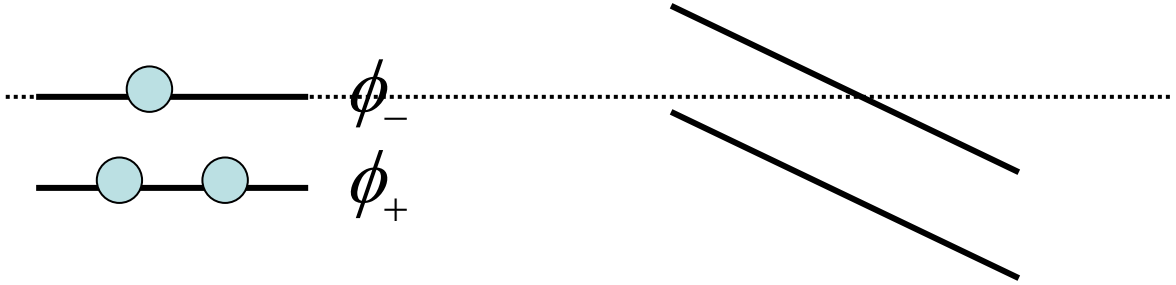



Isolated $Ni(tmdt)_2$

Solid $Ni(tmdt)_2$

½ filled
2 orbitals/cell

**Band width > HOMO – LUMO gap**

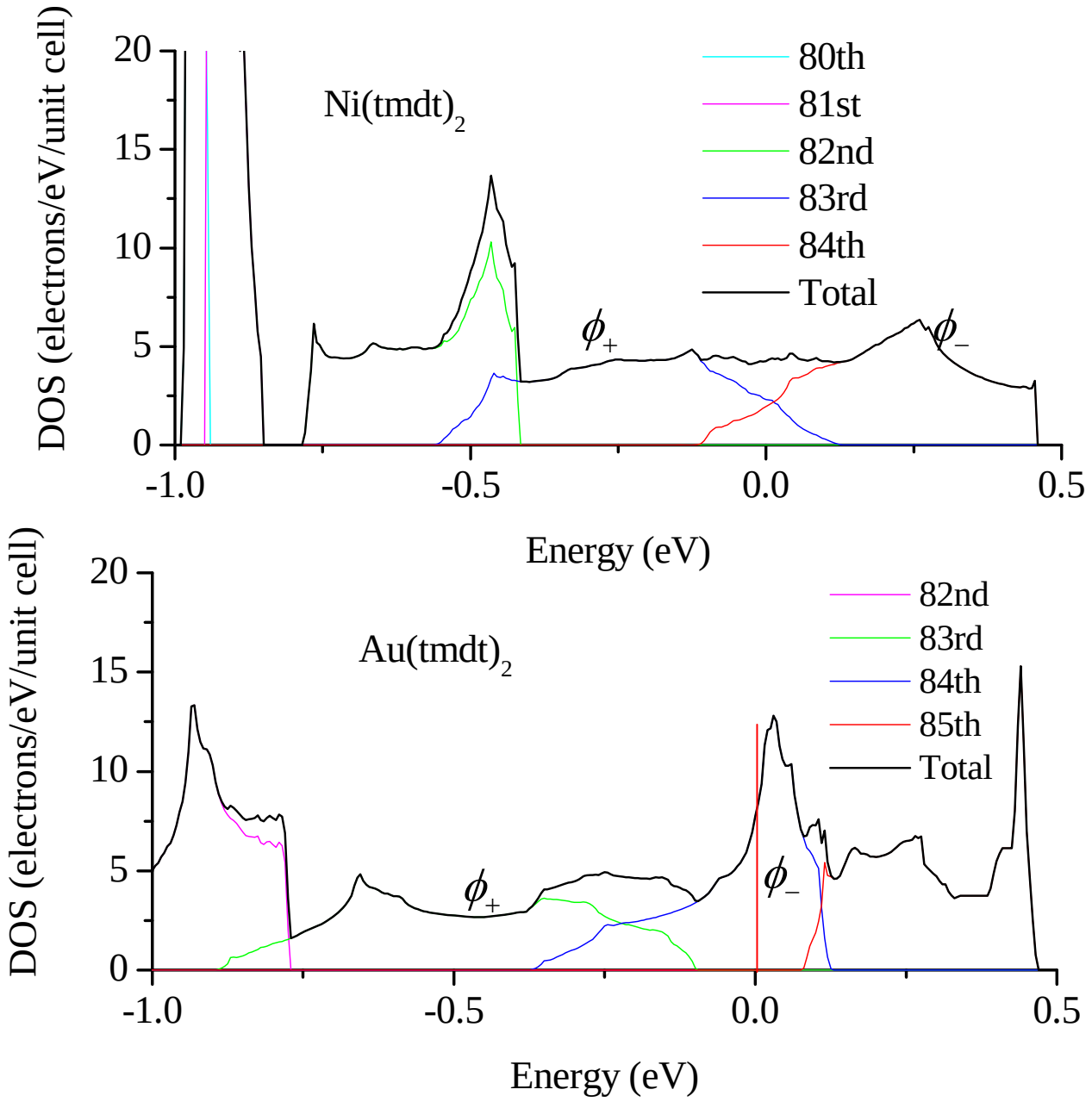



Isolated $Au(tmdt)_2$

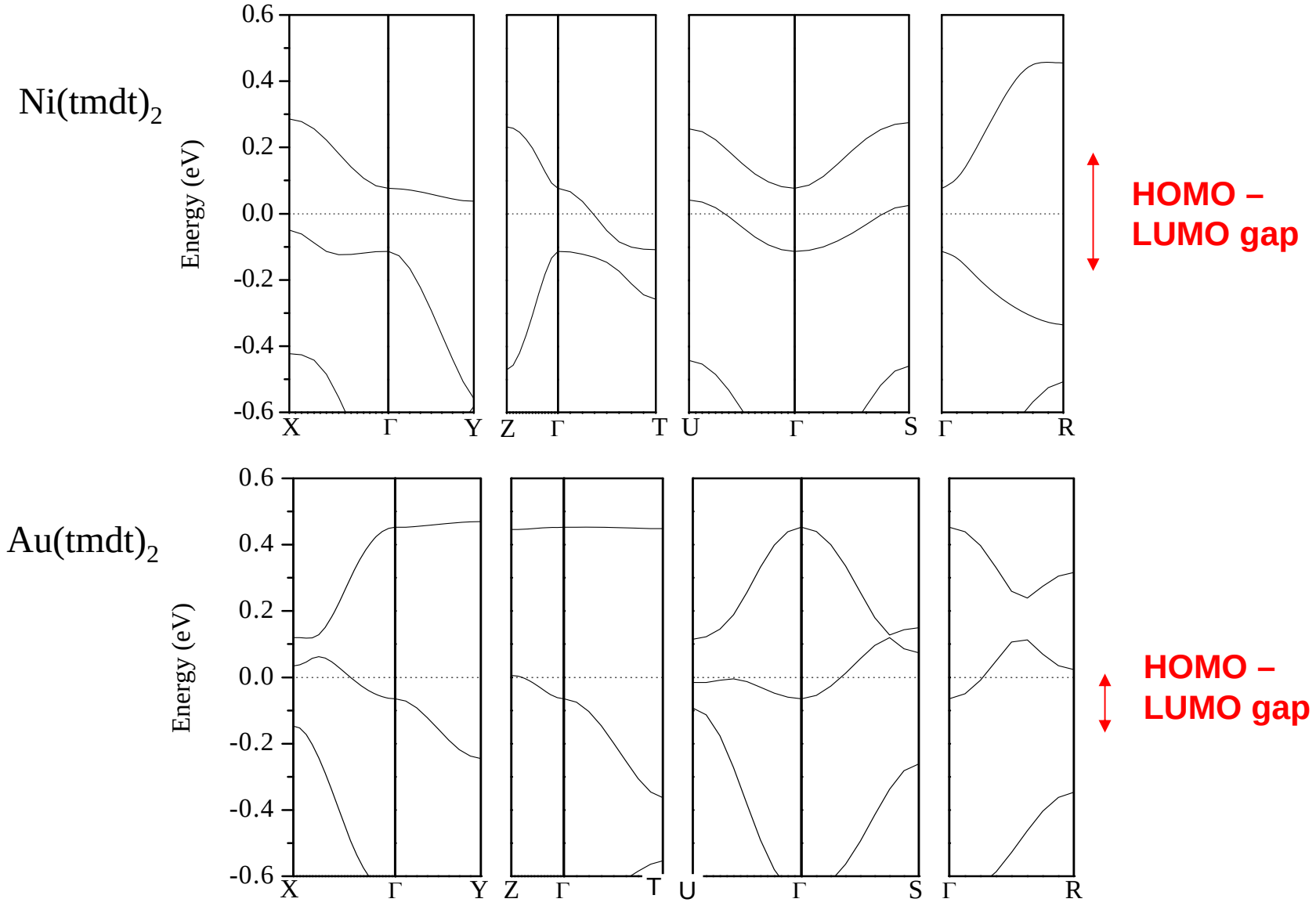
Solid $Au(tmdt)_2$

¾ filled
4 orbitals/cell in AFM

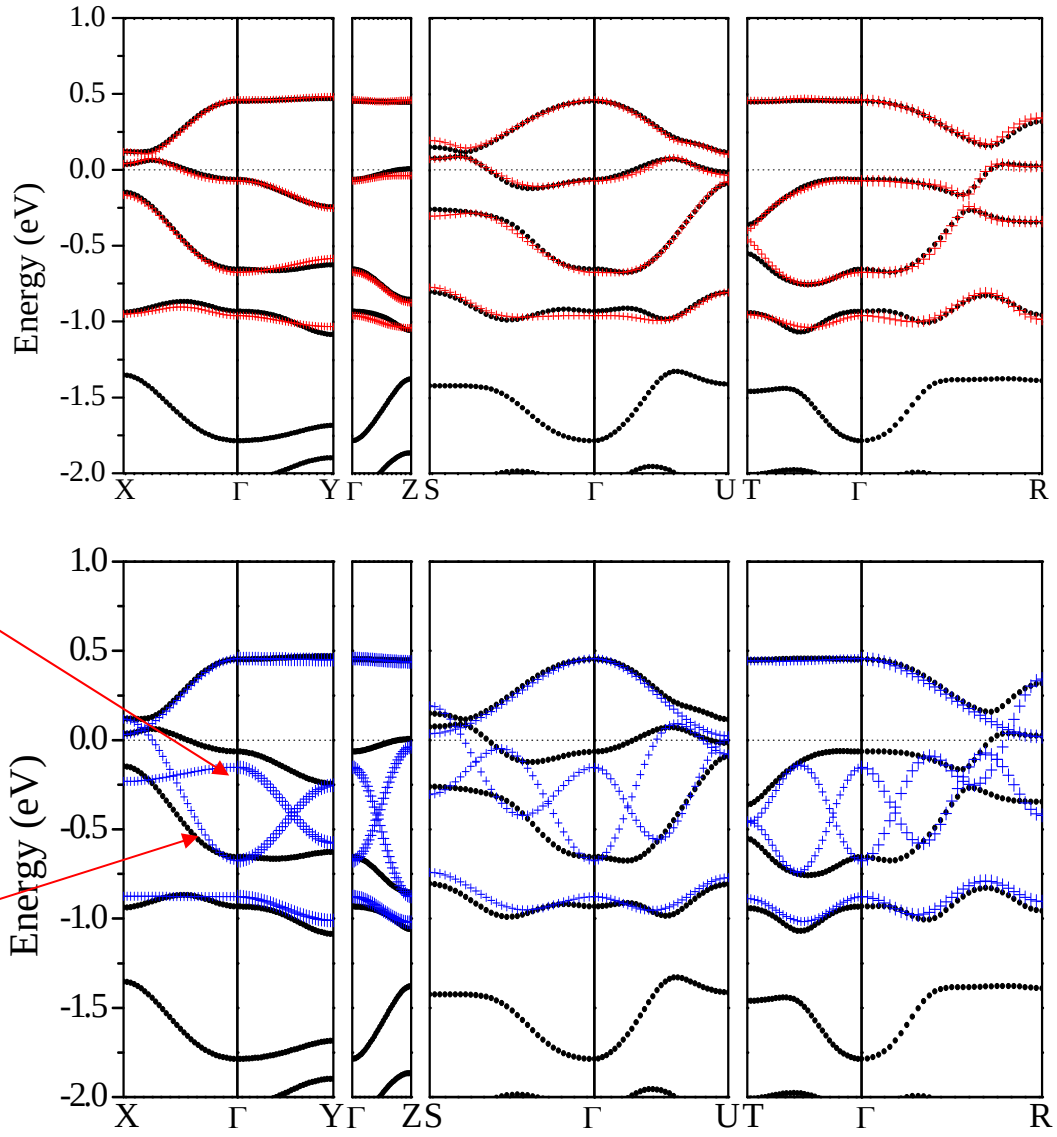
**0.5 e / リガンドの π 軌道**




Comparison of density of states for $Ni(tmdt)_2$ and $Au(tmdt)_2$




Band dispersion for $Ni(tmdt)_2$ and $Au(tmdt)_2$




**HOMO-HOMO**

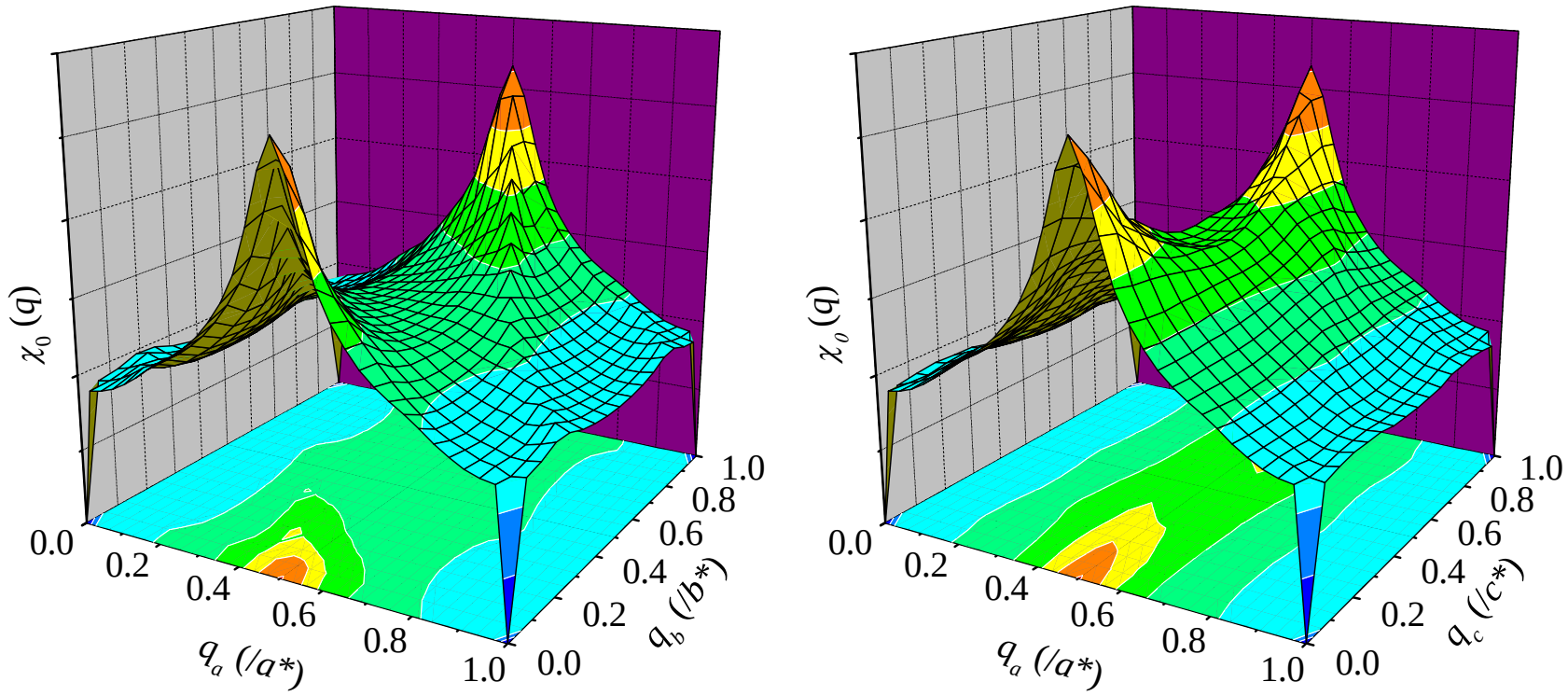
**without homo-lumo hybridization**

**LUMO-LUMO**

分子内の
リガンド間の
カップリングが
弱い。

X(1/2,0,0), Y(0,1/2,0), Z(0,0,1/2),

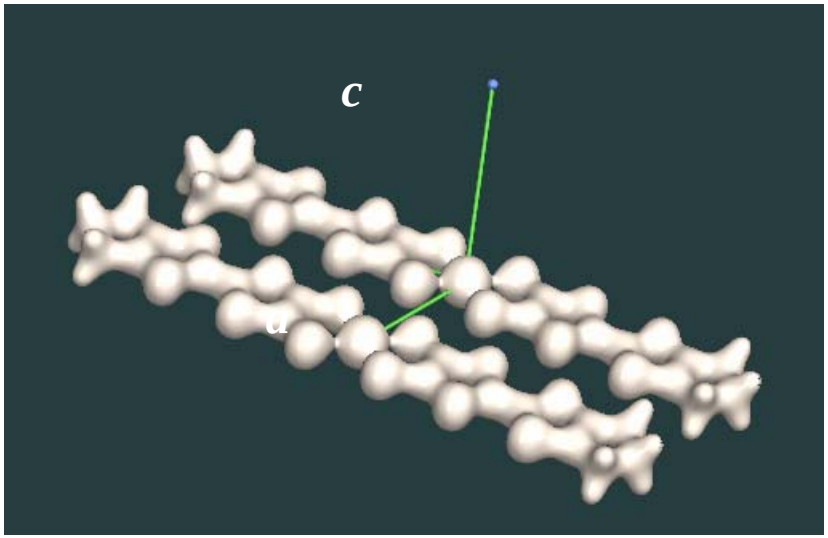
S(1/2,1/2,0), U(1/2,0,1/2), T(0,1/2,1/2), R(1/2,1/2,1/2)

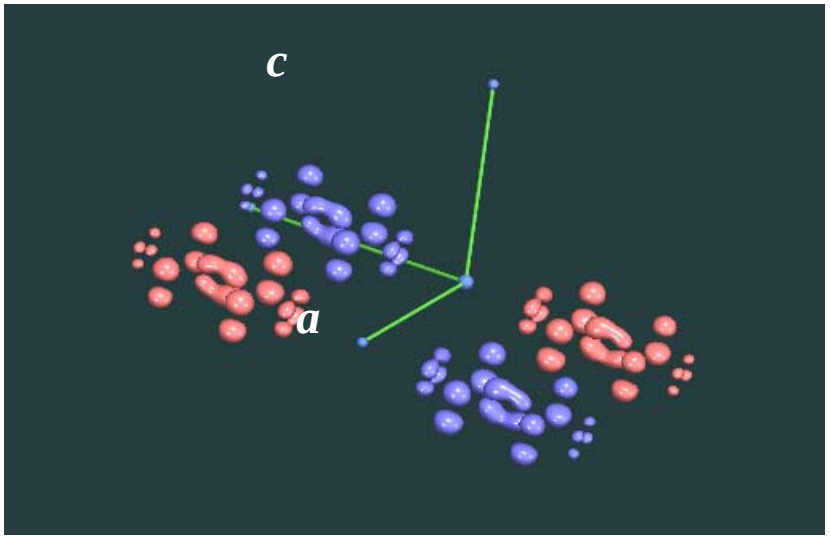


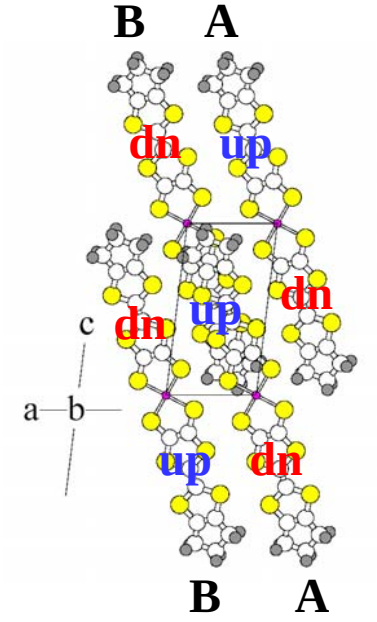

$$\chi_0(\mathbf{q}) = \int_{BZ} \frac{f\left(E_n(\mathbf{k})\right)\left[1 - f\left(E_n(\mathbf{k}+\mathbf{q})\right)\right]}{E_n(\mathbf{k}+\mathbf{q}) - E_n(\mathbf{k})} d\mathbf{k} \quad \text{for } Au(tmdt)_2$$

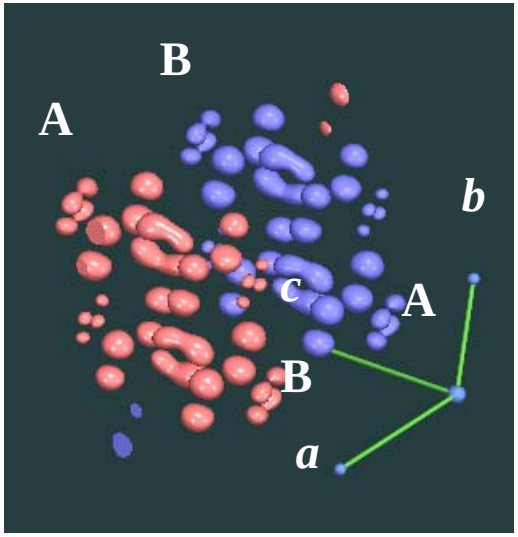
charge density

spin density: intra-molecular AF
no spin density on Au




spin-polarized GGA

Unit cell: $2\boldsymbol{a} \times \boldsymbol{b} \times \boldsymbol{c}$

$\rho_{\text{down}}(\mathbf{r}) = \rho_{\text{up}}(\boldsymbol{r}+\boldsymbol{a})$

Magnetic moment: $0.08\,\mu_B$

The energy difference between NM and AFM phases is almost zero.

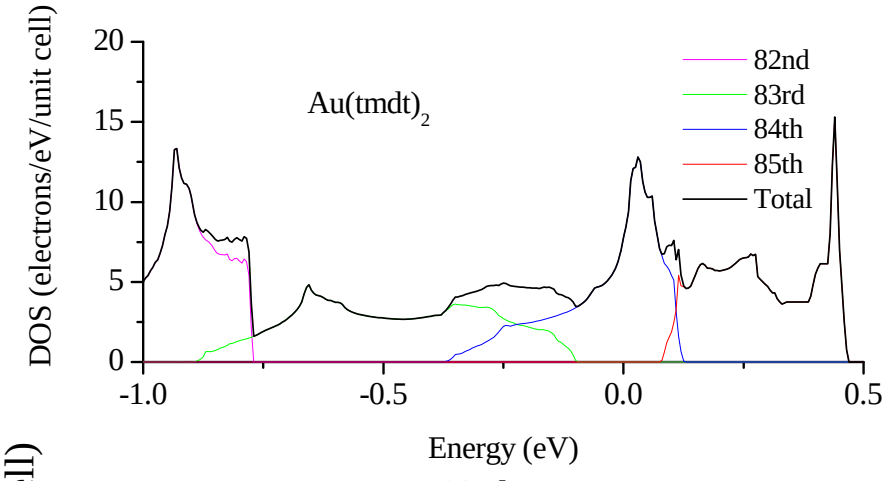
Spin density in $Au(tmdt)_2$

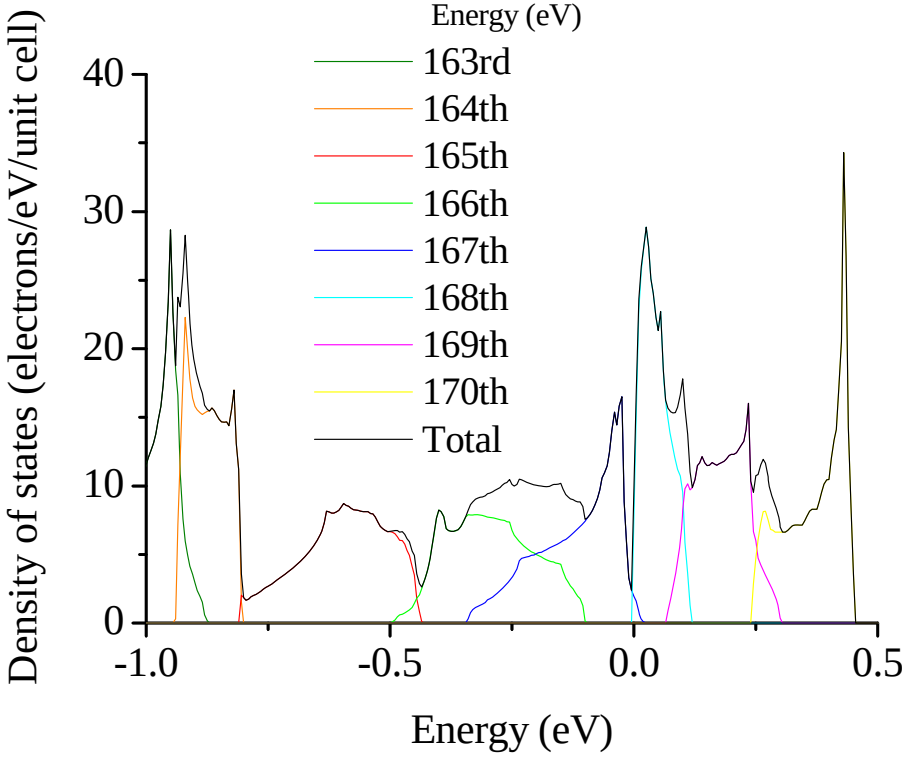
**non-mag**

**antiferro**

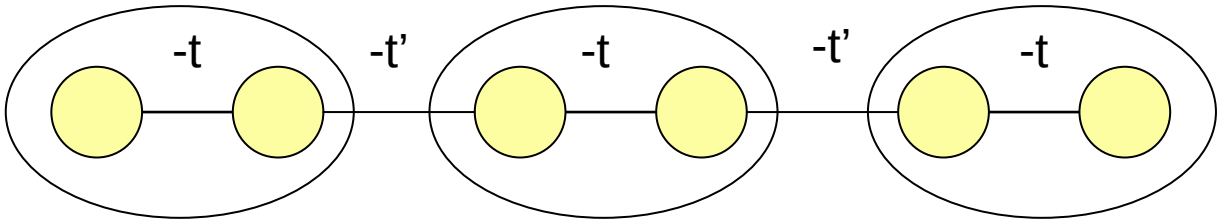
**for about 0.3 $\mu_B$**

**artificially enhanced xc potential by factor 1.05**



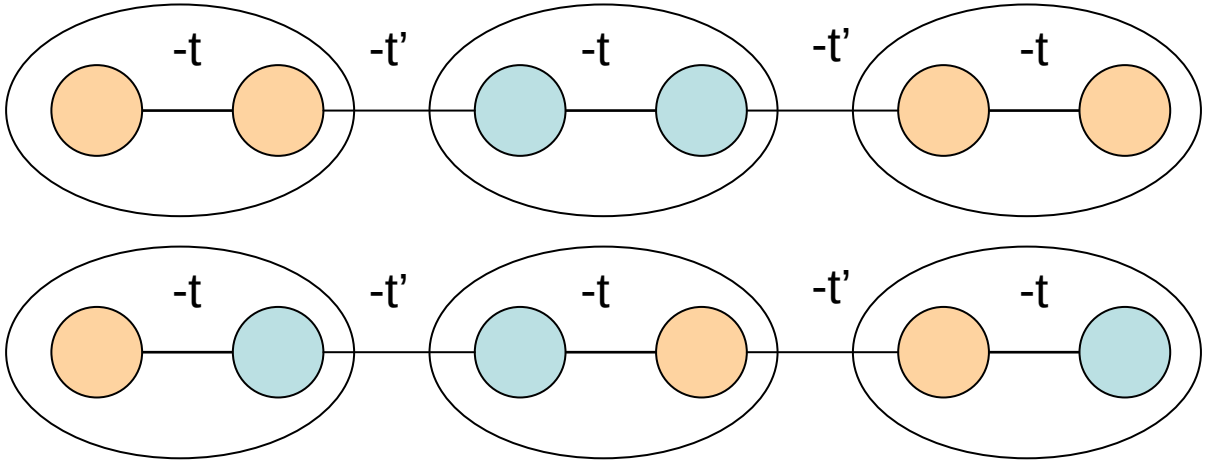



# Why intra-molecular AF spin distribution in AF state in $Au(tmdt)_2$




molecule

Two possible AF configurations



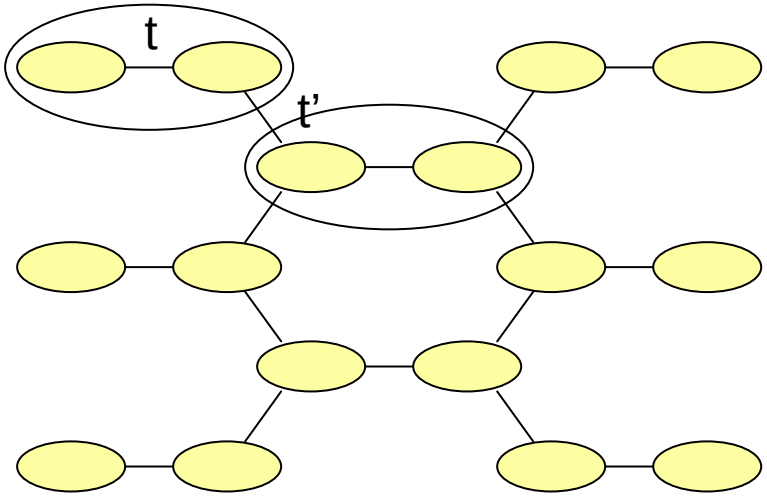

or

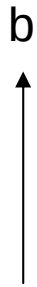
probably

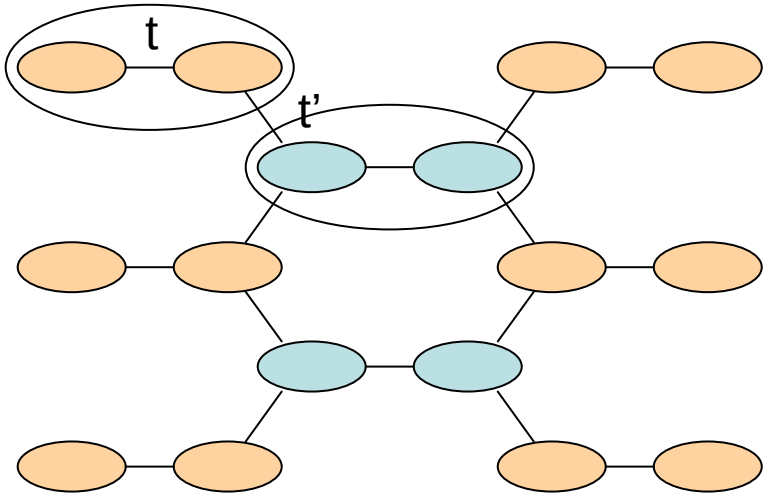
**t > t'**

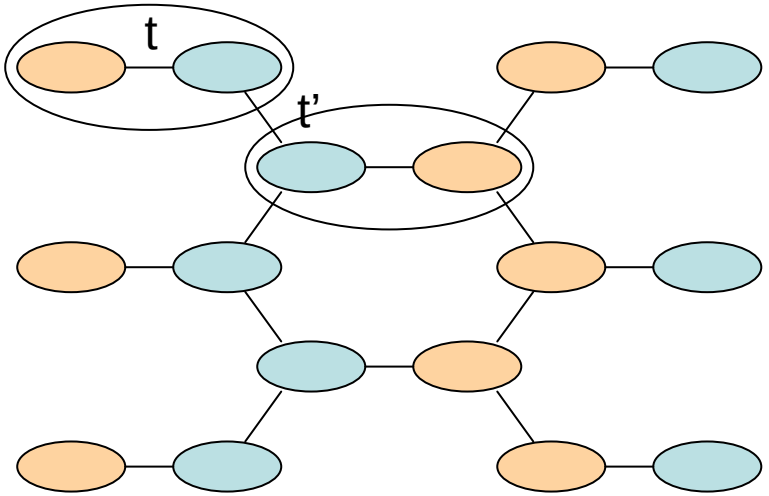
**t < t'**

**Case of $Au(tmdt)_2$**


t
t’


b


t
t’


t
t’

small contribution from d orbitals

**t' > t :** due to the character of $\pi$ orbitals of ligand and the stacking of molecules

band width

HOMO – LUMO gap

$Ni(tmdt)_2$

Overlap of HOMO and LUMO bands

semimetallic nature

$Au(tmdt)_2$

Intramolecular AF spin density distribution

# physical properties of Au(tmdt)2

- **Pauli paramagnetic susceptibility**

$$\chi = 2\mu_B^2 D(\varepsilon_F)$$

DOS in states/eV/spin/formula unit

$$= 6.5\times10^{-5}\times D$$ **in emu/mol**

D is about 5 in paramagnetic state.
Then $\chi$ is about 3.3 x $10^{-4}$ emu/mol.
The experimental value is about 4.2 x $10^{-4}$ emu/mol

- **Why is $T_N$ so high?**

probably due to strong short range order

プロトンNMRとは矛盾？

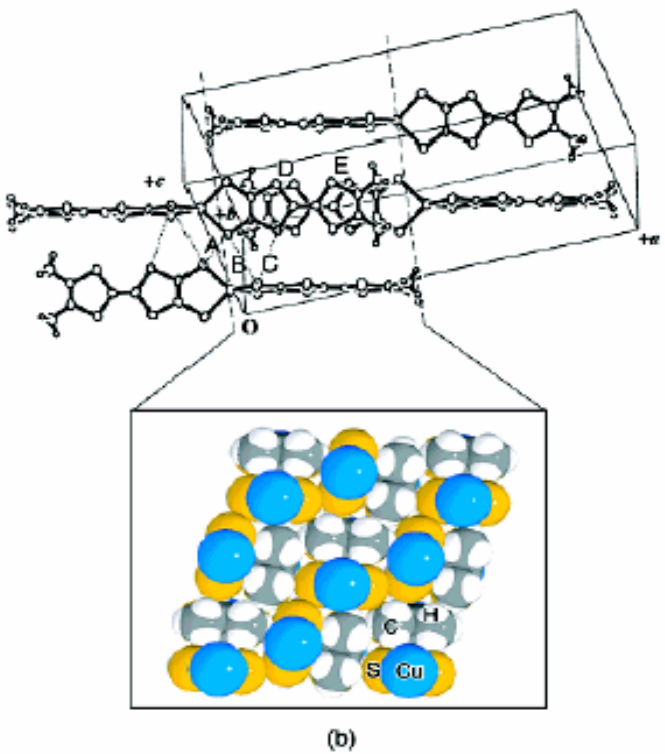



*Figure 1.* (a) Molecular structure of dianion copper complex in **2**. (b) Molecular arrangement of **1**. The lower part of figure presents the arrangement of ligand moieties projected along the molecular long axis. The S···S contacts are shown as dotted lines. A: 3.45 Å, B: 3.69 Å, C: 3.73 Å, D: 3.70 Å, E: 3.66 Å.

$Cu(dmdt)_2$ :

H. Tanaka *et al.*, JACS **124**, 10002 (2002).

$a$ = 24.24 Å, $b$ = 8.250 Å, $c$ = 11.500 Å

β= 91.38 ° , $V$ = 2299. Å$^3$, Z=4

**semiconductor (?) $E_a$ = 0.04 eV**

84% of S=1/2 spin

$Zn(tmdt)_2$ :

K. Yamamoto *et al.*, Chem. Lett. **34**, 1090 (2005).

$a$ = 25.33 Å, $b$ = 8.067 Å, $c$ = 11.36 Å

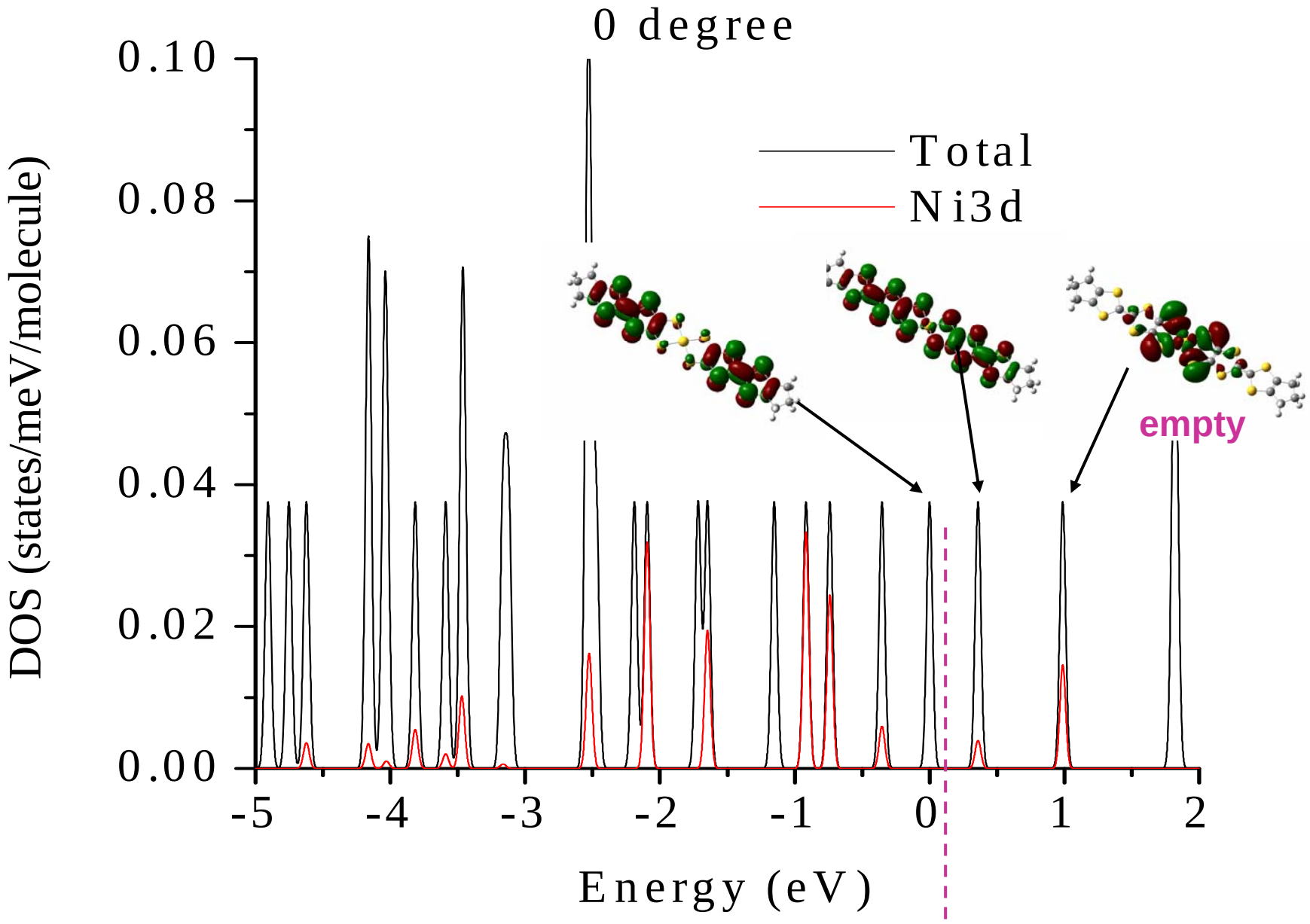
$\beta$ = 92.71 ° , $V$ = 2319. Å$^3$, Z=4

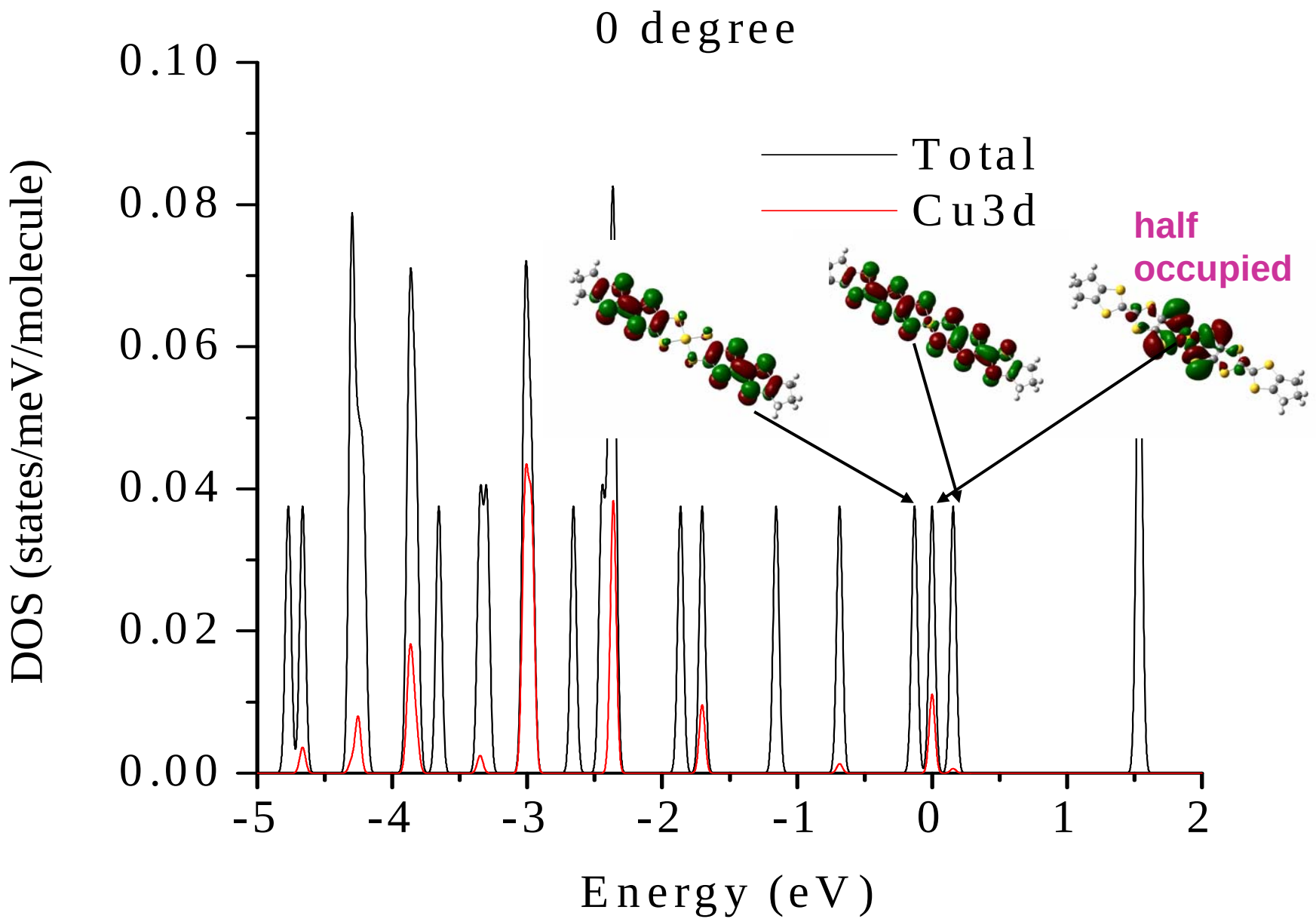
**semiconductor (?) $E_a$ = 0.15 eV**

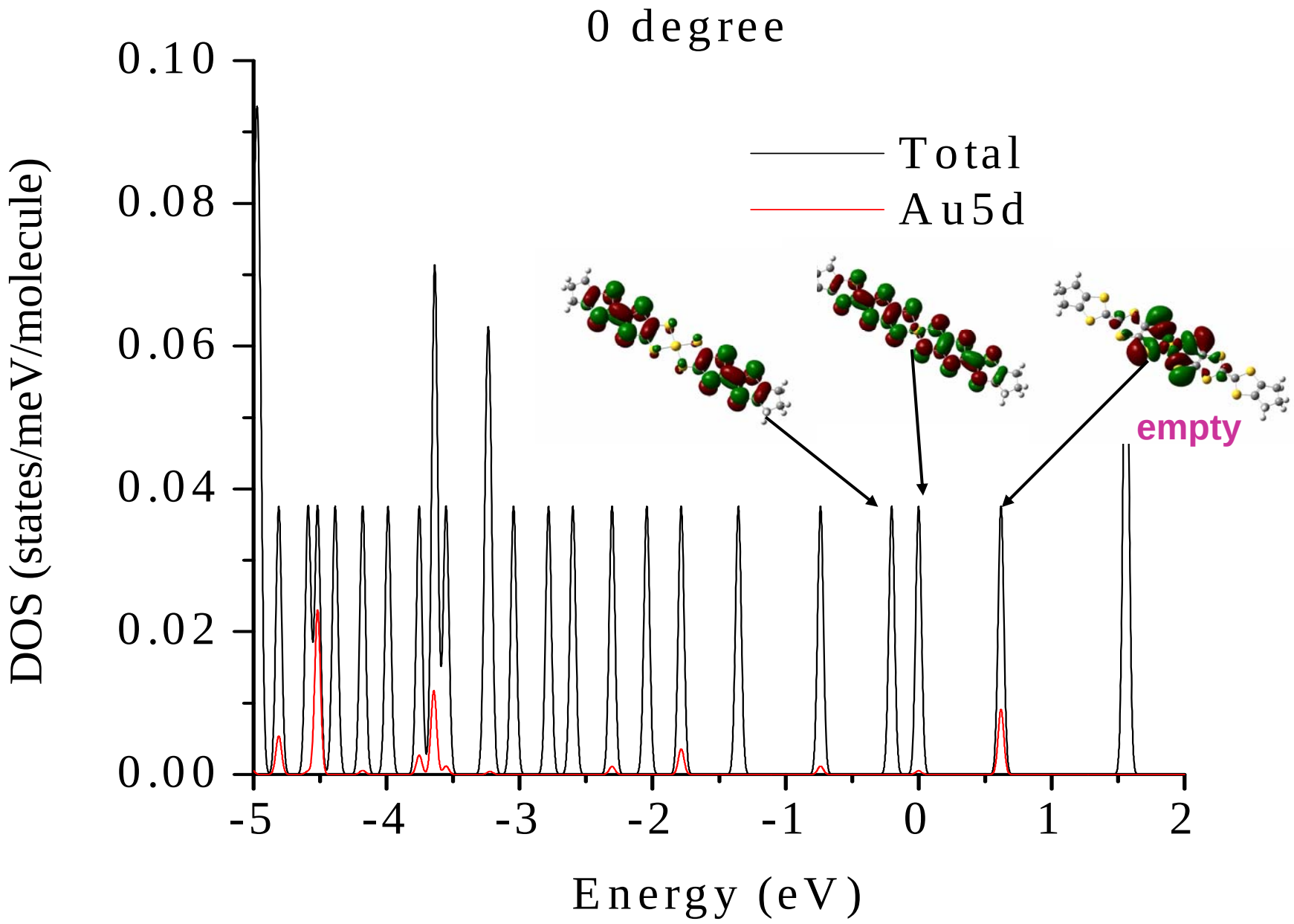
temperature-independent paramagnetism

Space group C2/c

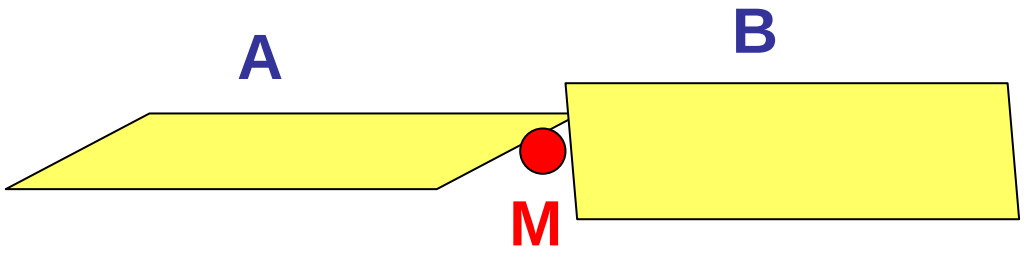
# Crystal structure of $Cu(dmdt)_2$ and $Zn(tmdt)_2$

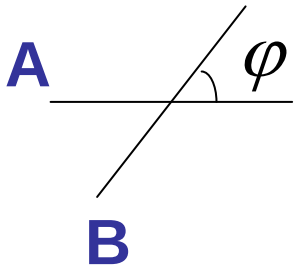

0 degree
Total
Ni3d
empty
DOS (states/meV/molecule)
0.10
0.08
0.06
0.04
0.02
0.00
-5
-4
-3
-2
-1
0
1
2
Energy (eV)


0 degree
Total
Cu3d
half
occupied
DOS (states/meV/molecule)
0.10
0.08
0.06
0.04
0.02
0.00
-5
-4
-3
-2
-1
0
1
2
Energy (eV)

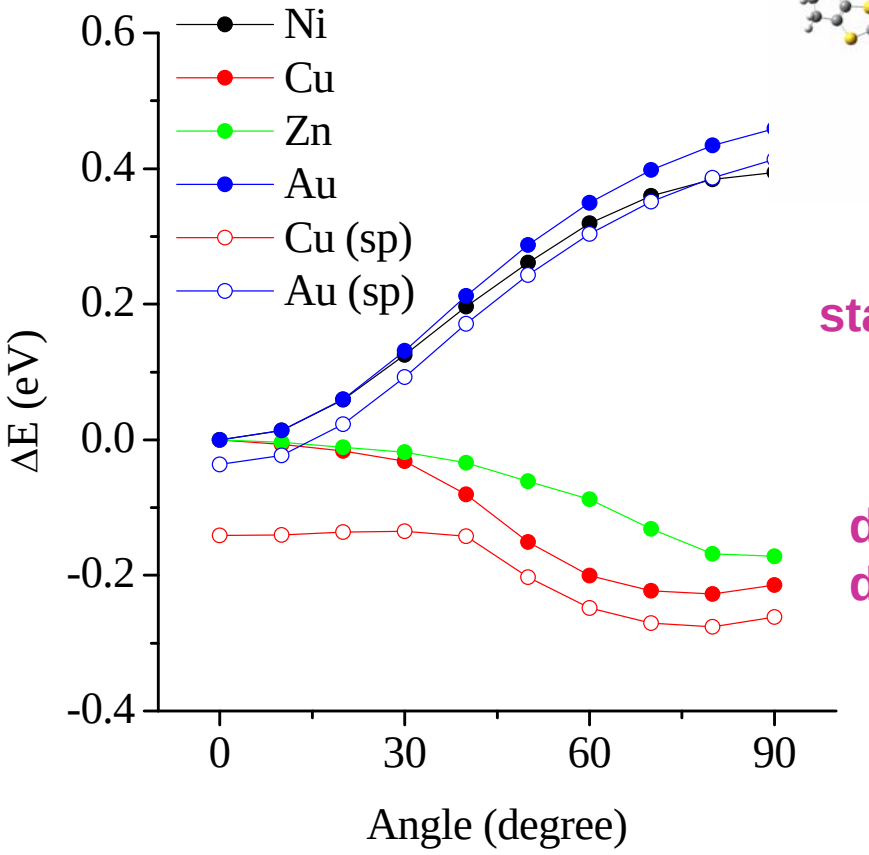

0 degree
Total
Au5d
empty
DOS (states/meV/molecule)
0.10
0.08
0.06
0.04
0.02
0.00
-5
-4
-3
-2
-1
0
1
2
Energy (eV)

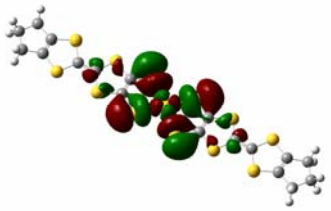
# twisting of ligand molecules




$\varphi$ : 0.0 ° for M = Ni, Au
80.29 ° for M = Cu
89.63 ° for M = Zn



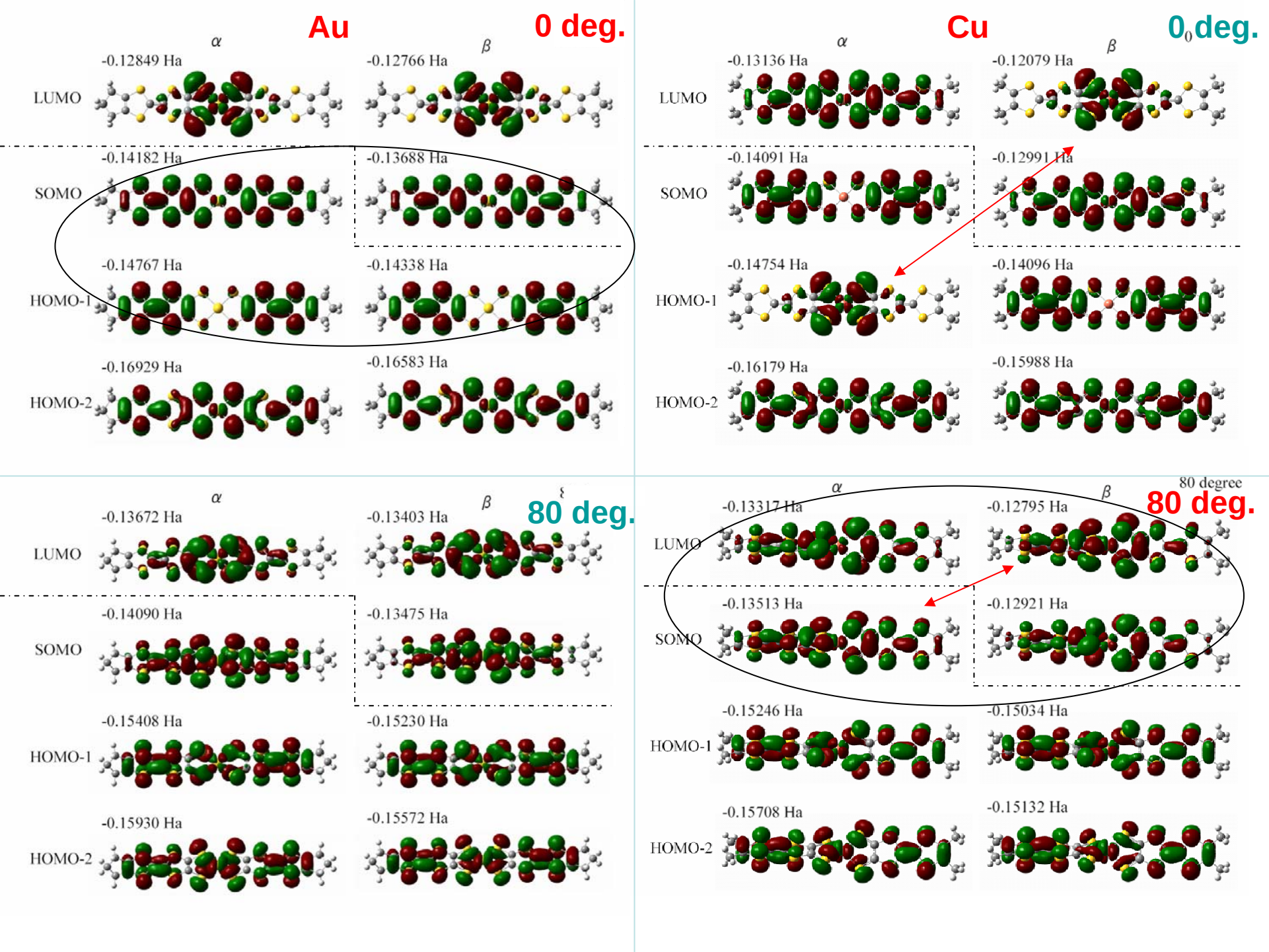



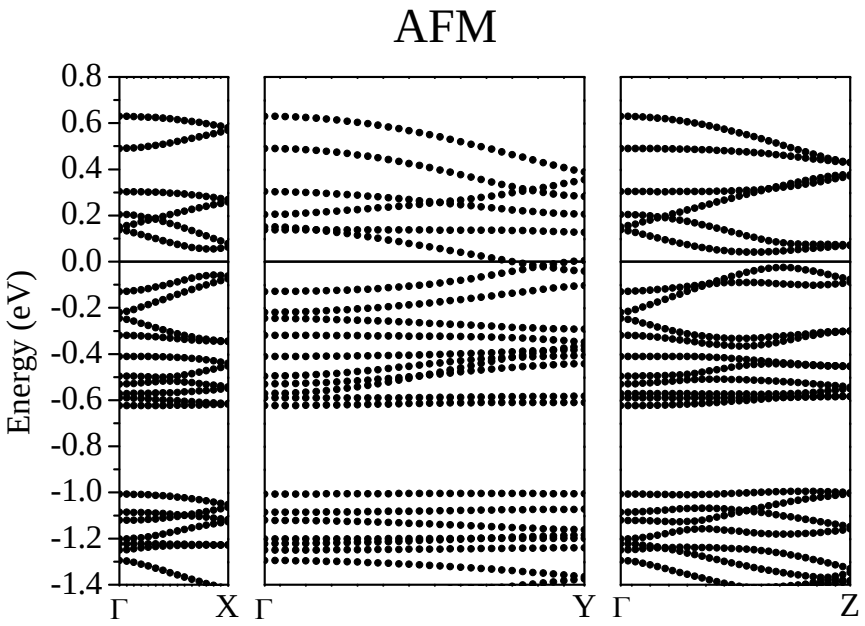
: empty

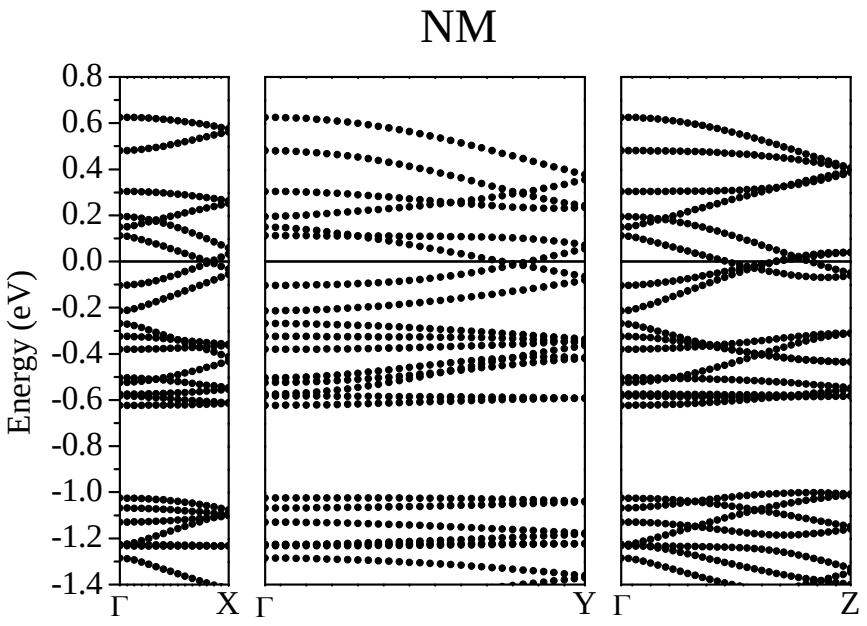
stability of planar structure

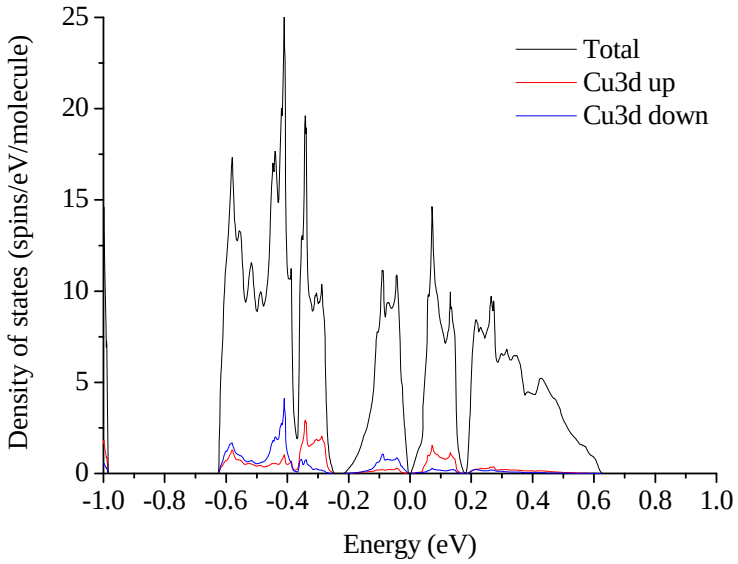
deviation from 90 degree
due to Jahn-Teller effect

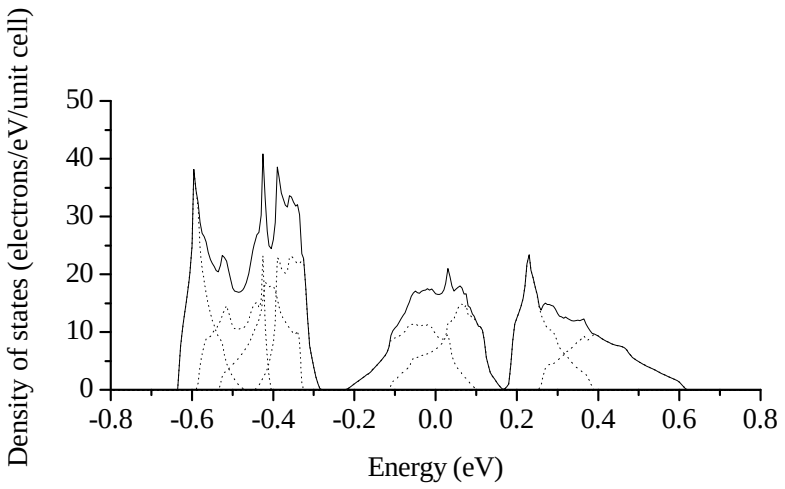
qmas_gammaで計算しなおした、角度-エネルギー変化の関係
(原子位置は面内で最適化。各分子のエネルギーの基準は、スピン偏極無しの0度のもの。)


Au
0 deg.
α
β
LUMO
-0.12849 Ha
-0.12766 Ha
SOMO
-0.14182 Ha
-0.13688 Ha
HOMO-1
-0.14767 Ha
-0.14338 Ha
HOMO-2
-0.16929 Ha
-0.16583 Ha
Cu
0 deg.
LUMO
-0.13136 Ha
-0.12079 Ha
SOMO
-0.14091 Ha
-0.12991 Ha
HOMO-1
-0.14754 Ha
-0.14096 Ha
HOMO-2
-0.16179 Ha
-0.15988 Ha
80 deg.
LUMO
-0.13672 Ha
-0.13403 Ha
SOMO
-0.14090 Ha
-0.13475 Ha
HOMO-1
-0.15408 Ha
-0.15230 Ha
HOMO-2
-0.15930 Ha
-0.15572 Ha
80 degree
80 deg.
LUMO
-0.13317 Ha
-0.12795 Ha
SOMO
-0.13513 Ha
-0.12921 Ha
HOMO-1
-0.15246 Ha
-0.15034 Ha
HOMO-2
-0.15708 Ha
-0.15132 Ha


AFM
Energy (eV)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Γ
X
Γ
Y
Γ
Z


NM
Energy (eV)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Γ
X
Γ
Y
Γ
Z


Density of states (spins/eV/molecule)
25
20
15
10
5
0
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
Energy (eV)
Total
Cu3d up
Cu3d down


Density of states (electrons/eV/unit cell)
50
40
30
20
10
0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
Energy (eV)

# $Cu(dmdt)_2$

# questions to be answered

- reason for metallicity for Ni- & Au- $(tmdt)_2$
- AF configuration of $Au(tmdt)_2$
- reason for high $T_N$ for $Au(tmdt)_2$
- reason for weak anomaly in resistivity at $T_N$
- effects of substitution in ligand
- different molecular conformation

  $Au(tmdt)_2$ is planar while $Cu(dmdt)_2$ is twisted.
- why no magnetic long-range order for $Cu(dmdt)_2$ despite the presence of localized moment on Cu?

赤字は未解決

殆ど判ってない！