Inorganic Chemistry Laboratory,
Department of Chemistry,
University of Oxford

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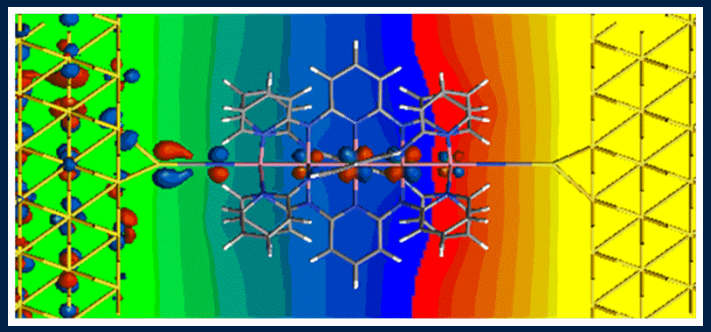
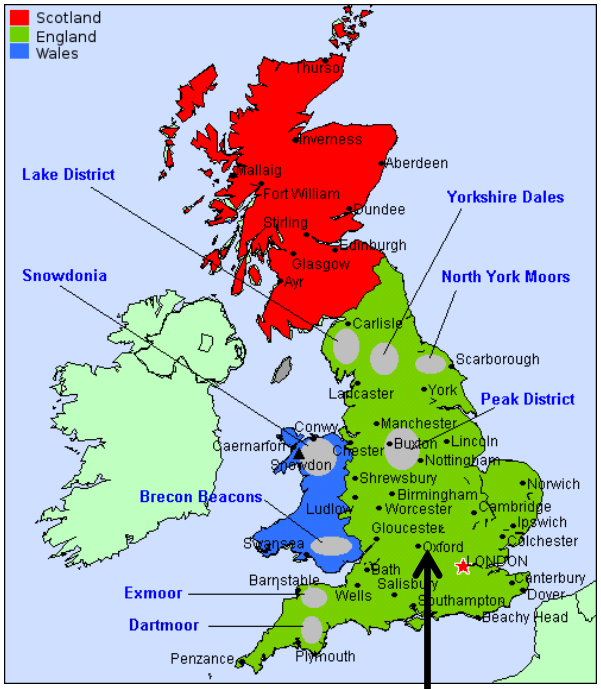
Molecular Wires: from metal-metal bonds to electron transport



John McGrady, University of Oxford

March 14, 2013 Peking University, Beijing


Scotland
England
Wales
Thurso
Inverness
Aberdeen
Mallaig
Fort William
Dundee
Stirling
Edinburgh
Glasgow
Ayr
Lake District
Snowdonia
Yorkshire Dales
North York Moors
Peak District
Brecon Beacons
Exmoor
Dartmoor
Carlisle
Scarborough
Lancaster
York
Conwy
Manchester
Caernarfon
Chester
Buxton
Lincoln
Sherydon
Nottingham
Shrewsbury
Norwich
Birmingham
Ludlow
Worcester
Cambridge
Ipswich
Gloucester
Colchester
Swansea
Oxford
LONDON
Bath
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Dover
Southampton
Beachy Head
Penzance
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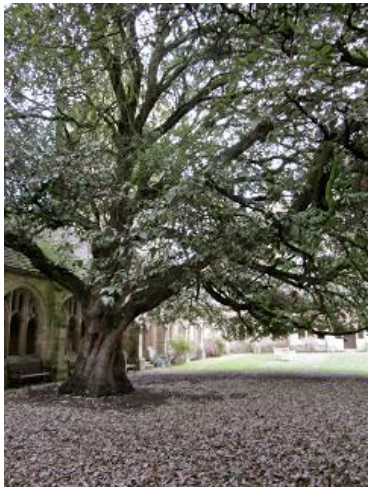
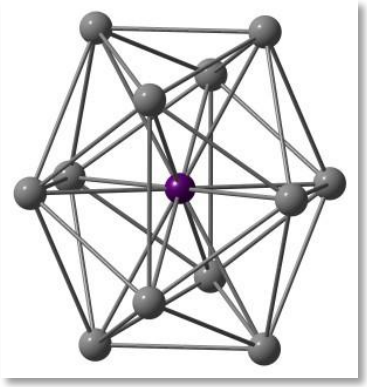
New College (founded 1379)

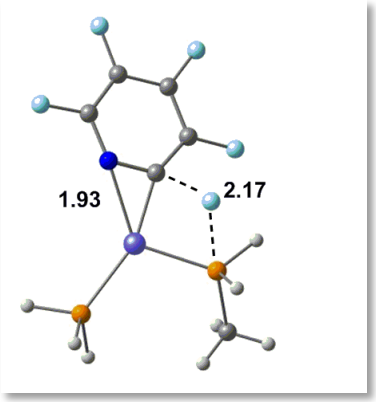


Computational Inorganic Chemistry

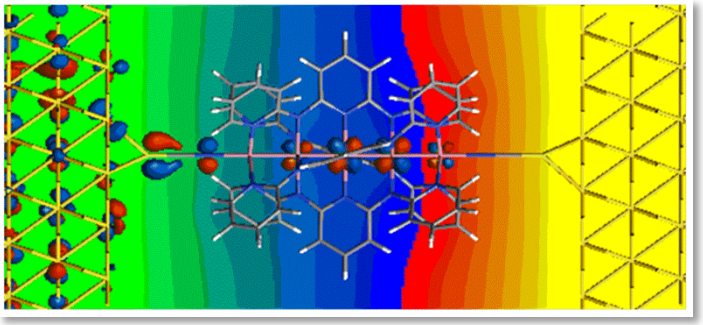
Zintl ions ($[Mn@Pb_{12}]^{3-}$)



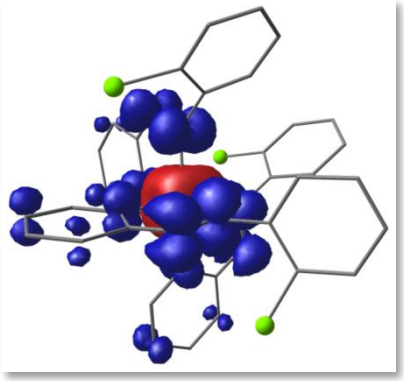
Organometallic reaction mechanisms



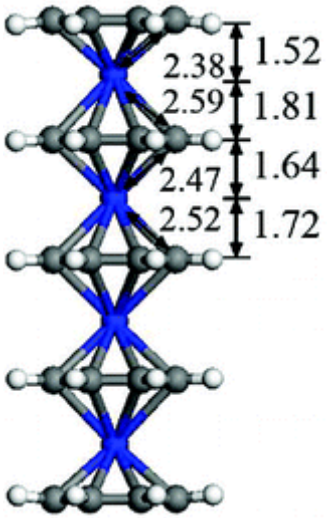
Molecular electronics



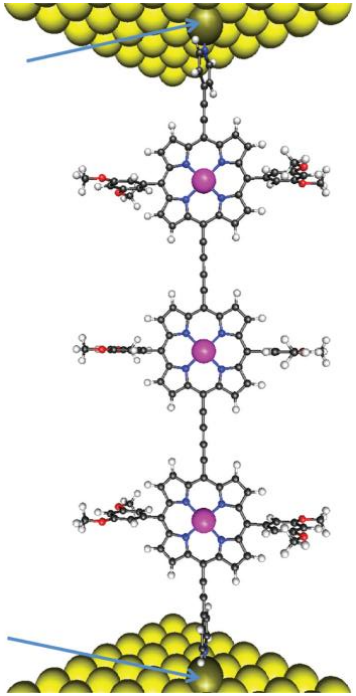
Non-innocent ligands



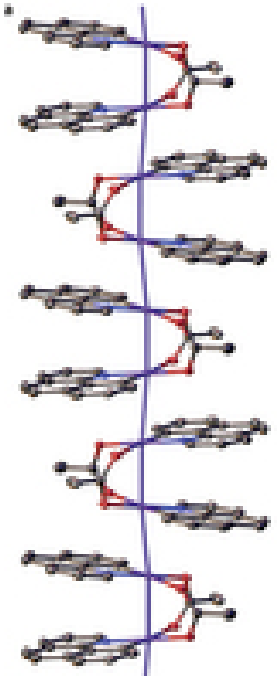
‘Molecular wires’



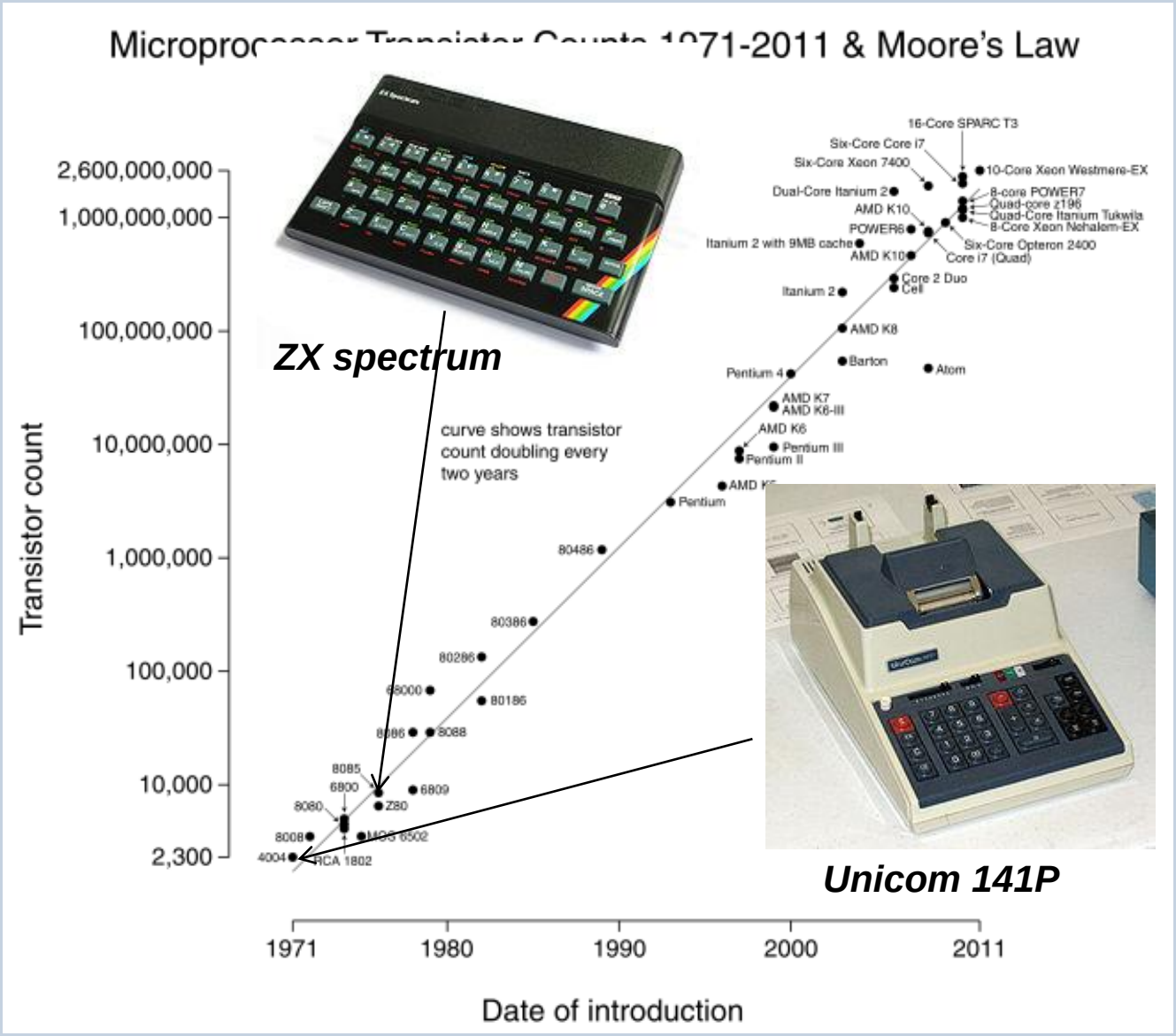
Fe COT derivatives:
Huang, Li *et al*.,
***J. Phys. Chem*., 2010.**

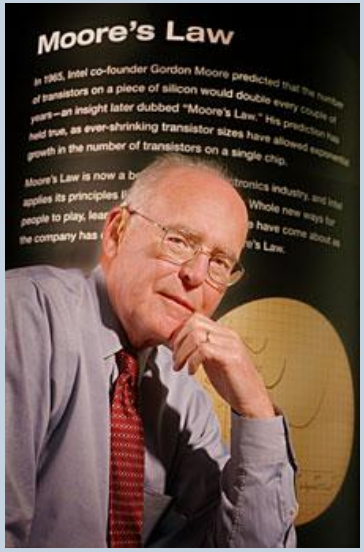


Zn porphyrins:
Anderson *et al*.,
***Nat. Nanotech.*, 2011.**

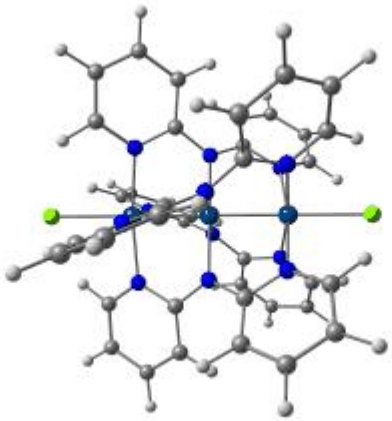


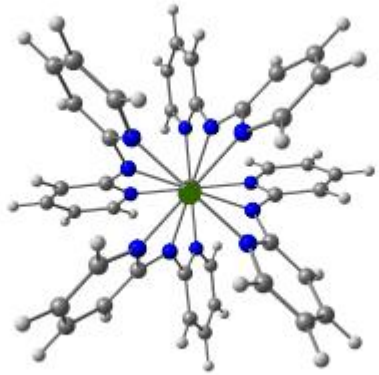
$(Pd^{2.5+})_{\sim 1000}$
Ritter,
***Nat. Chem*. 2011**


Microprocessor Transistor Counts 1971-2011 & Moore's Law
ZX spectrum
curve shows transistor count doubling every two years
Unicom 141P
Transistor count
2,600,000,000
1,000,000,000
100,000,000
10,000,000
1,000,000
100,000
10,000
2,300
16-Core SPARC T3
Six-Core Core i7
Six-Core Xeon 7400
10-Core Xeon Westmere-EX
Dual-Core Itanium 2
8-core POWER7
Quad-core z196
AMD K10
Quad-Core Itanium Tukwila
POWER6
8-Core Xeon Nehalem-EX
Itanium 2 with 9MB cache
Six-Core Opteron 2400
AMD K10
Core i7 (Quad)
Itanium 2
Core 2 Duo
Cell
AMD K8
Barton
Atom
Pentium 4
AMD K7
AMD K6-III
AMD K6
Pentium III
Pentium II
AMD K5
Pentium
80486
80386
80286
68000
80186
8086
8088
8085
6800
6809
8080
Z80
8008
MOS 6502
4004
RCA 1802
1971
1980
1990
2000
2011
Date of introduction


Moore's Law

*E*xtended *M*etal *A*tom *C*hains (EMACs): Cotton, Peng, Berry





Homotrimetallic: 1st row
Cr_3, Co_3, Ni_3, Cu_3

Homotrimetallic, 2nd/3rd rows
Ru_3, Rh_3

Heterotrimetallics
CoPdCo
W_2Fe
Mo_2Mn, Mo_2Fe, Mo_2Co
Cr_2Mn, Cr_2Fe, Cr_2Co, Cr_2Zn
CrMoW

Longer chains
$Cr_{5/7}$, $Co_{4/5/6/7}$, $Ni_{5/6/7/9/11}$
Ru_5
$NiRu_2Ni_2$

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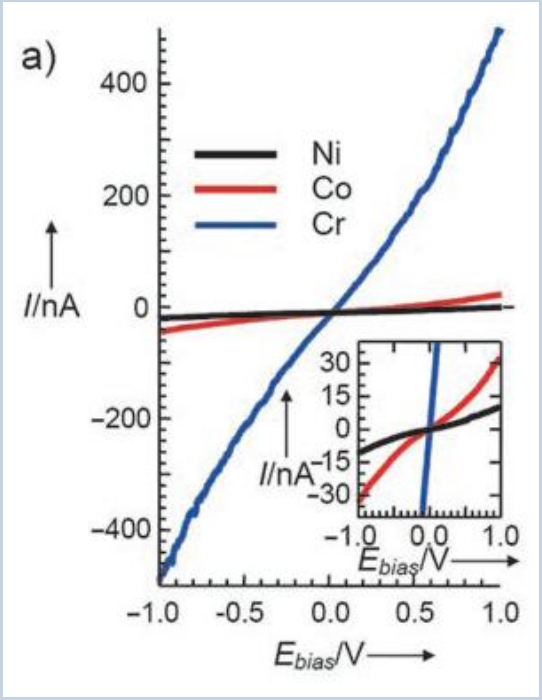
Experiments: trimetallic chains

STM

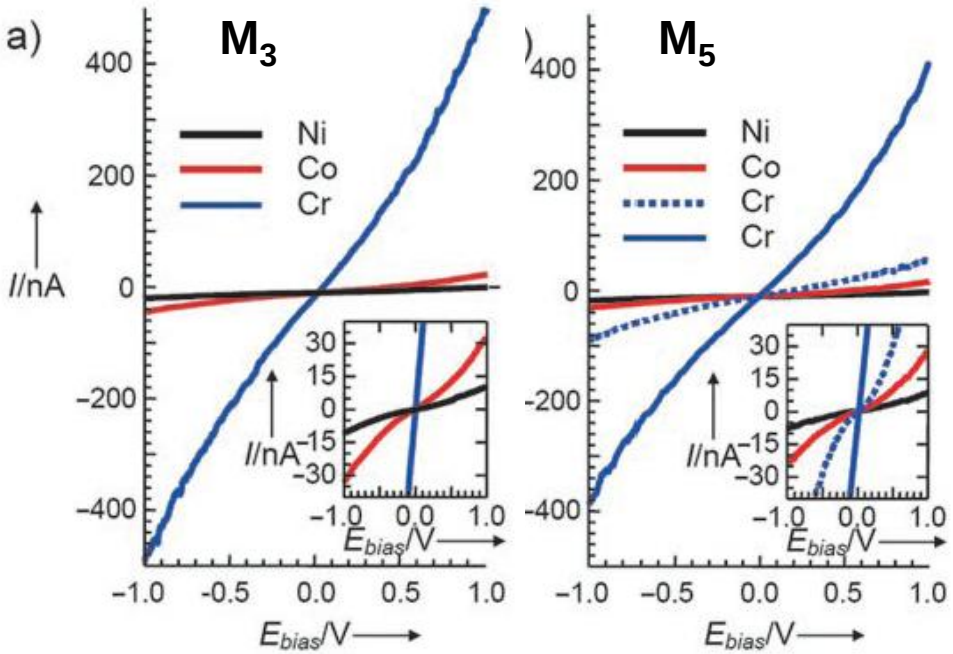


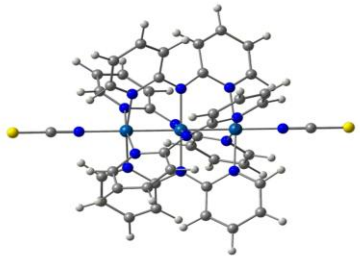
G/n*S*	STM	c-AFM
Cr_3	1110	370
Co_3	530	21
Ni_3	290	5.8
Ru_3	760	

$$G = \frac{1}{R} = \frac{\Delta I}{\Delta V}$$

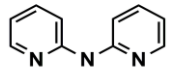
Peng, Chen *J. Phys. Chem. B* 2004, *108*, 959,
***Angew. Chem. Int. Ed.* 2006, *45*, 5814,**
***Chem Comm*., 2010, *46*, 1338.**

M_3 vs M_5 chains



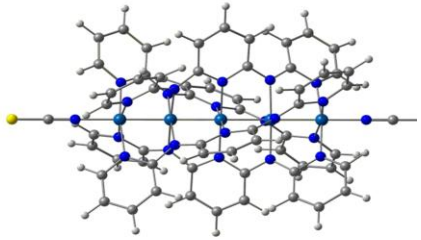


$Co_3(dpa)_4(NCS)_2$

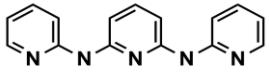


dpa

G* = 530 n*S



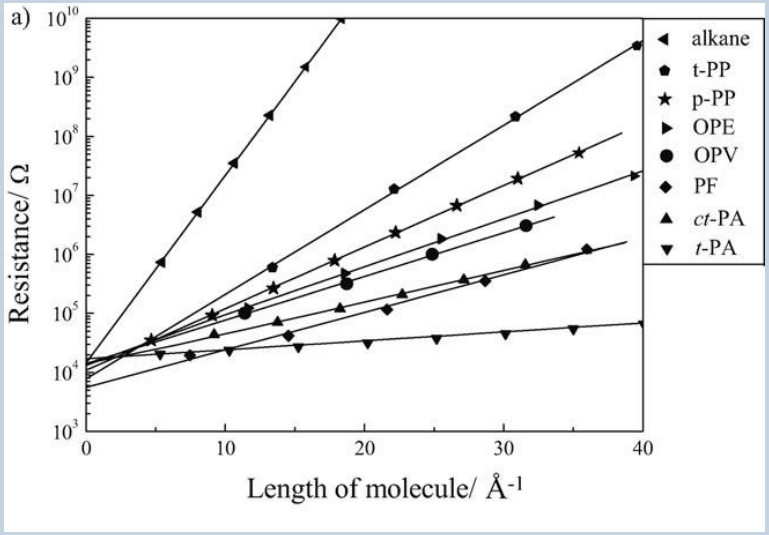
$Co_5(tpda)_4(NCS)_2$

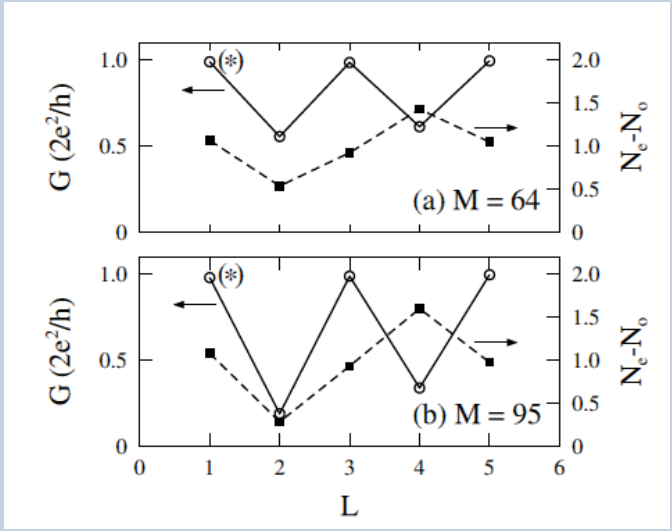


tpda

G* = 100 n*S

Models for length dependence:





Exponential decay:

$$R = R_c e^{-\beta r}$$

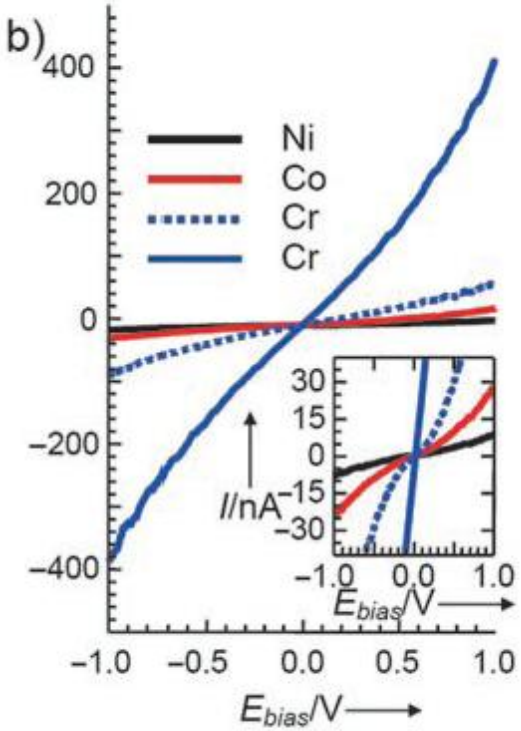
Zhao, *ChemPhysChem*, 2008.

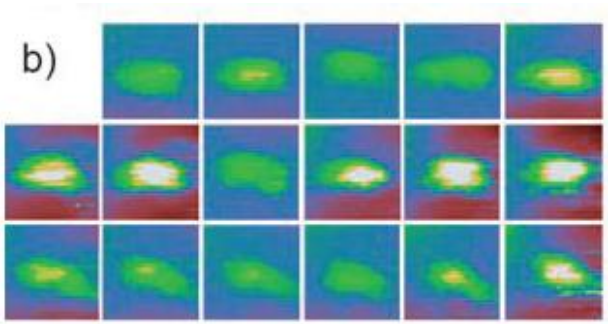
β ($Co_{3/5}$) = 0.2 Å^{-1}

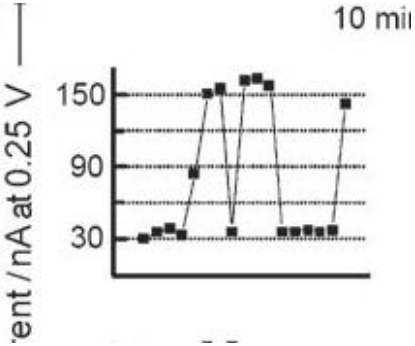
Odd-even oscillations in Na_x:

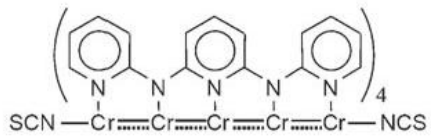
Sim, *PRL*, 2001.

M_5 chains

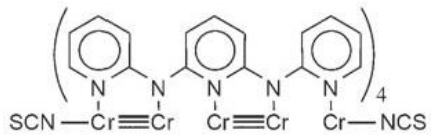








f)



'Stochastic switching'?

Questions:

What is the origin of the length dependence?

What is the origin of the differences between Co and Cr (is it really π bonding)?

Can low-symmetry distortions (bends, stretches) really 'break' the wires?

What is the relationship between 'delocalisation' and conductance in these systems?

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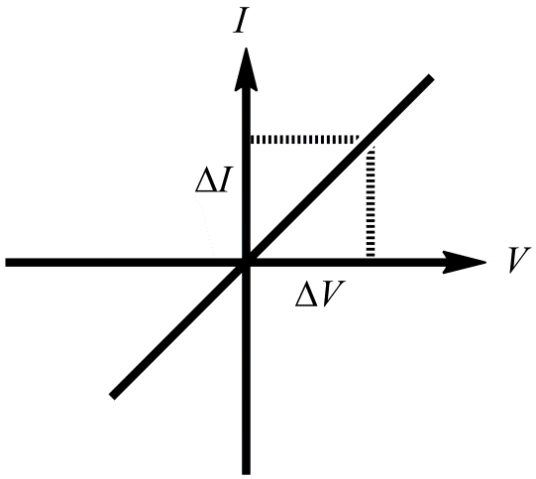
Current flow in macroscopic and nanoscale conductors:

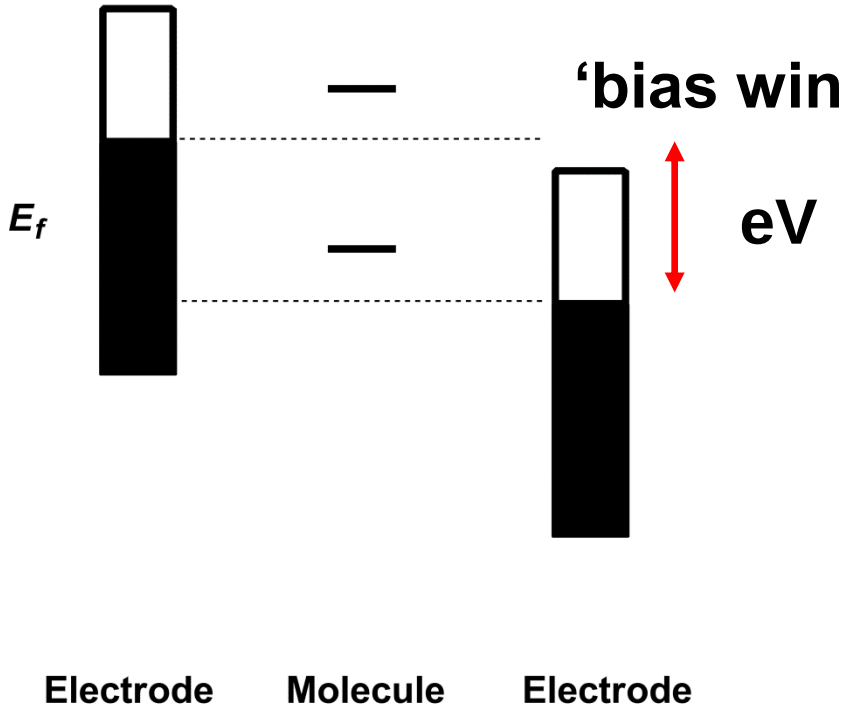


Ohm's law:

$$V \propto I$$

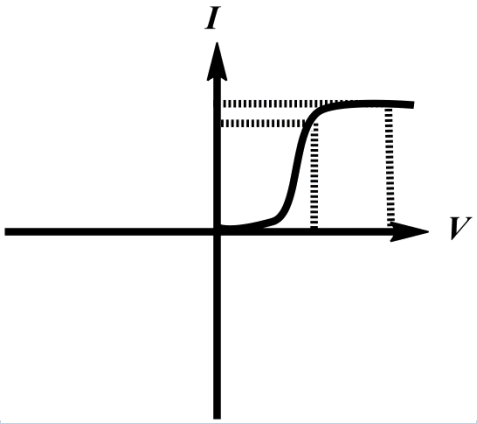
$$R = \frac{\Delta V}{\Delta I} \qquad G = \frac{1}{R} = \frac{\Delta I}{\Delta V}$$

Current flow in macroscopic and nanoscale conductors:



$$G_0 = 77nS$$

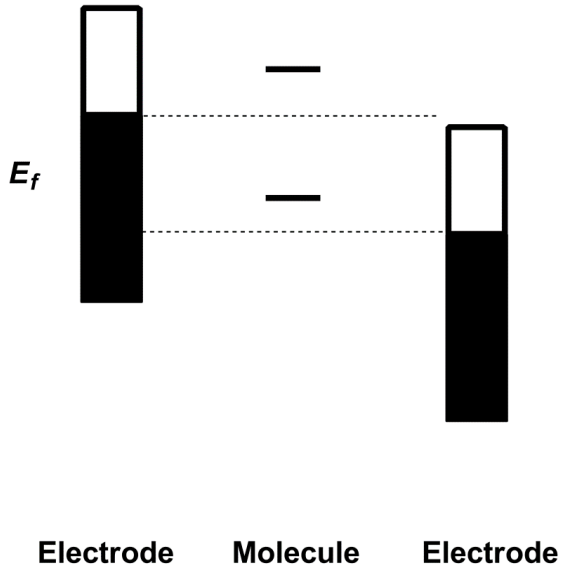
(quantum of conductance)



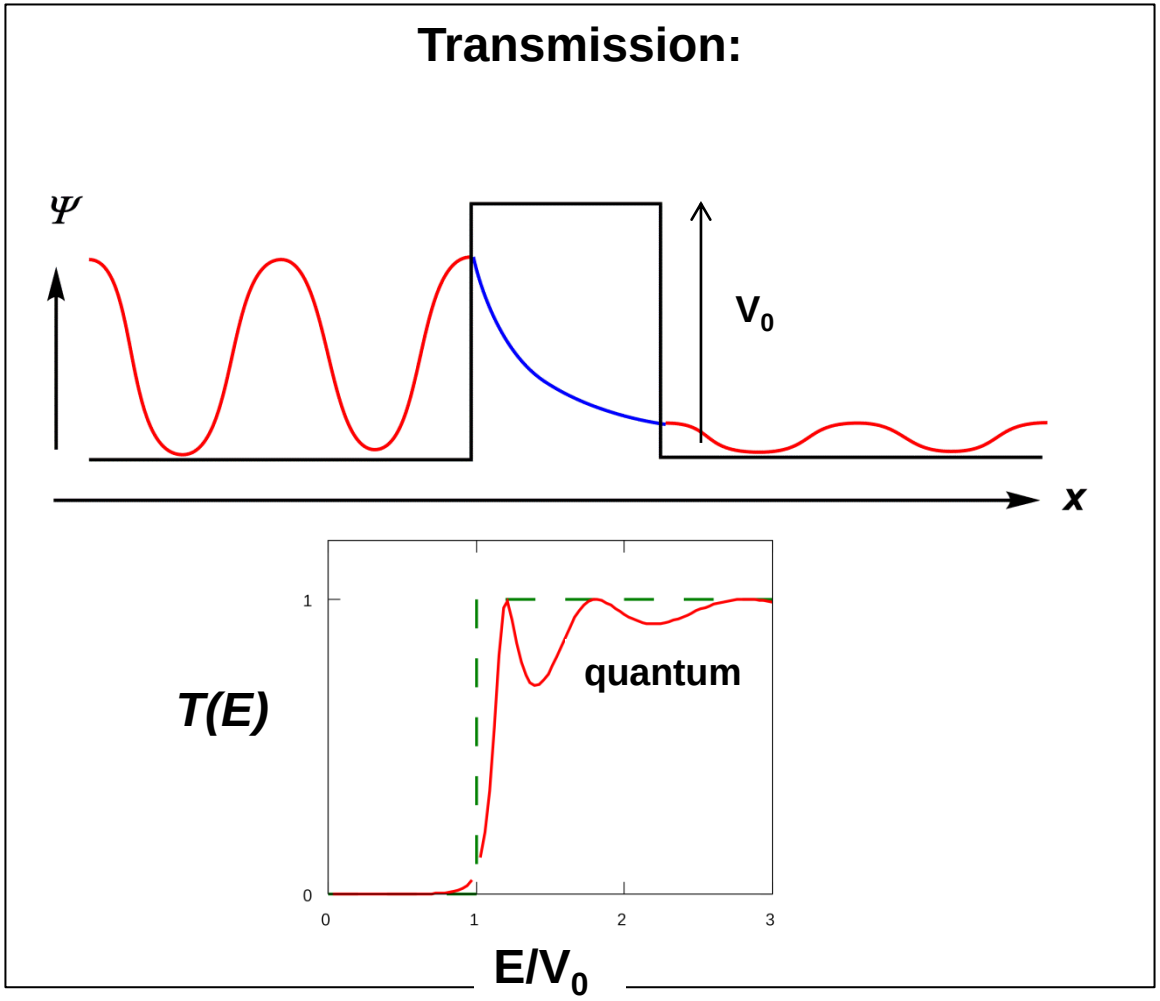
at finite T

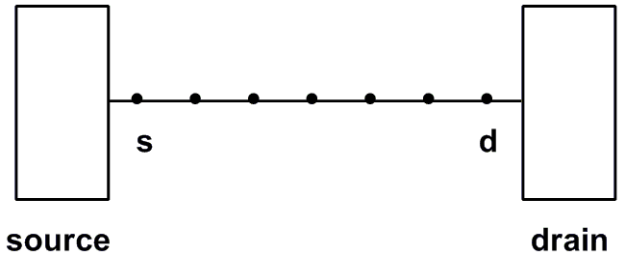
$$I(V,\sigma) = \frac{e}{h}\int_{-\infty}^{\infty} T(E,V)\left(f_L(E,V) - f_R(E,V)\right)dV$$

transparency **driving force**

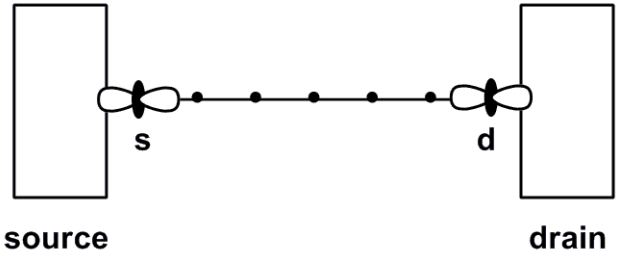


Transmission:

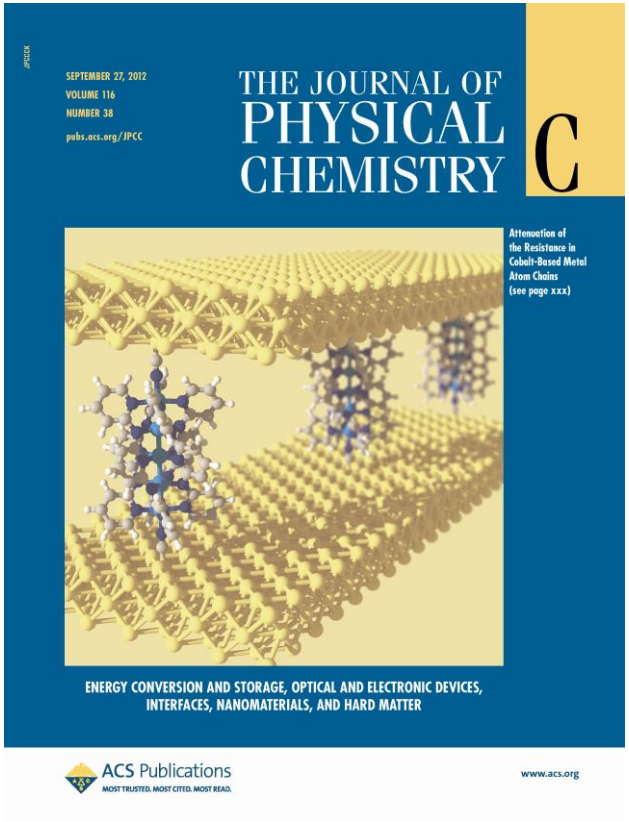




$$T(E) \approx \frac{4\alpha^2 \left(C_s\right)^2 \left(C_d\right)^2}{\left(E-\varepsilon\right)^2 + \alpha^2 \left(\left(C_s\right)^2 + \left(C_d\right)^2\right)}$$

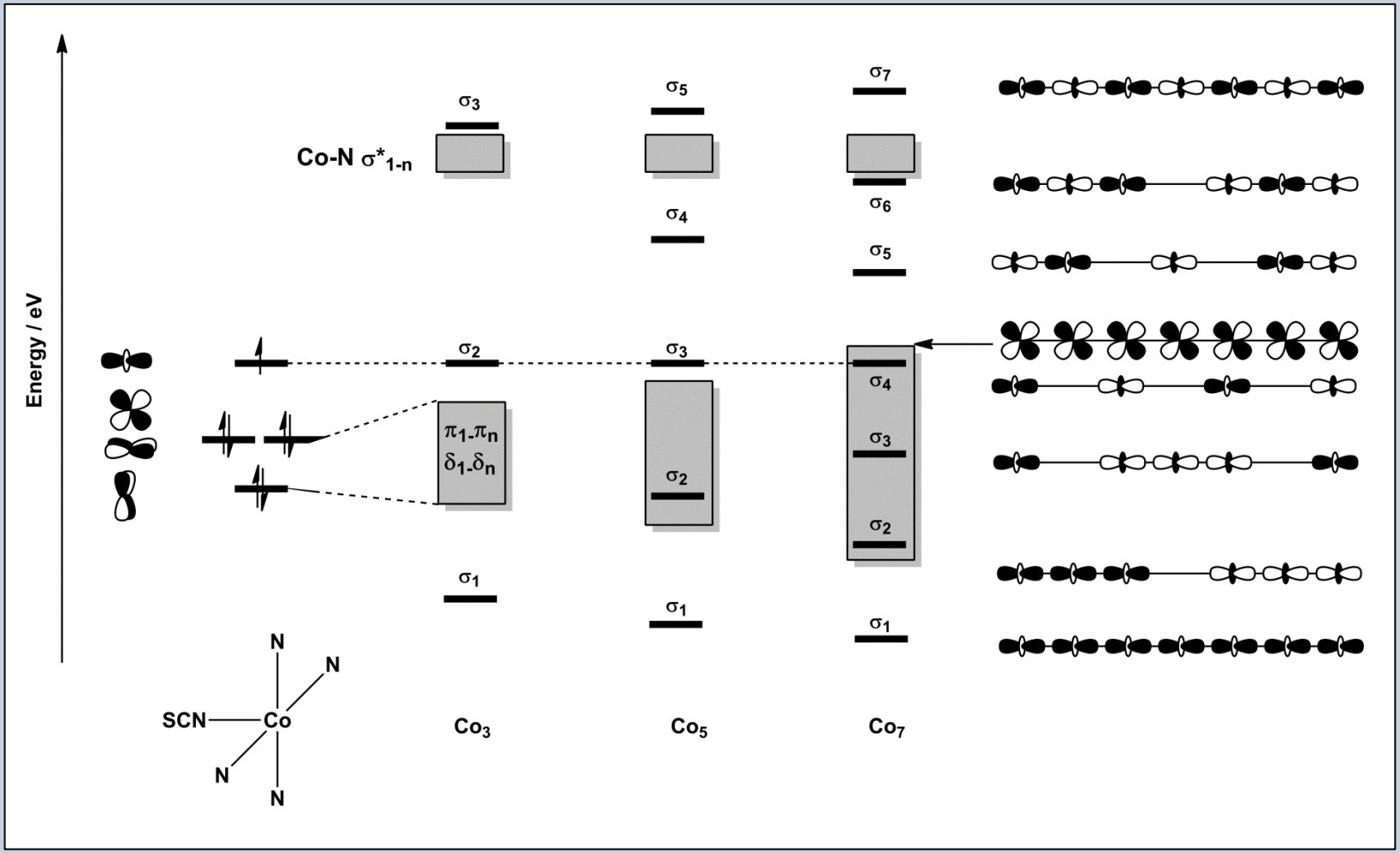


Methodology:

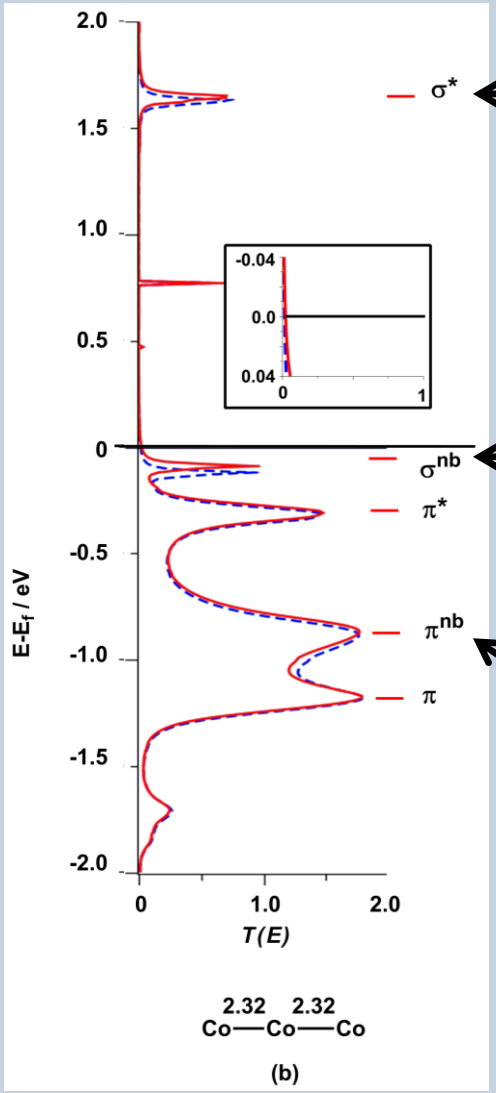


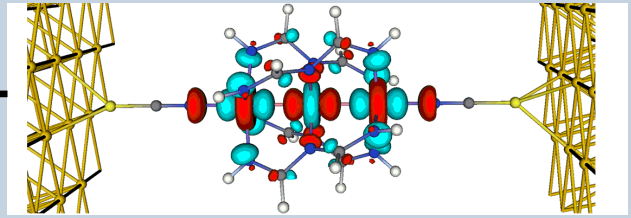
Transport calculations (LSDA+PZ): ATK2008/2010/2011 (NEGF)
Periodic boundary conditions perpendicular to transport direction (SIESTA)

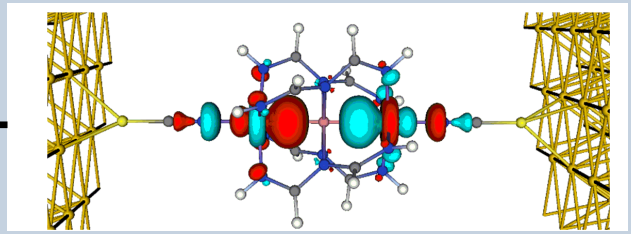
Co_n chains: 'the fruitfly' for transport calculations

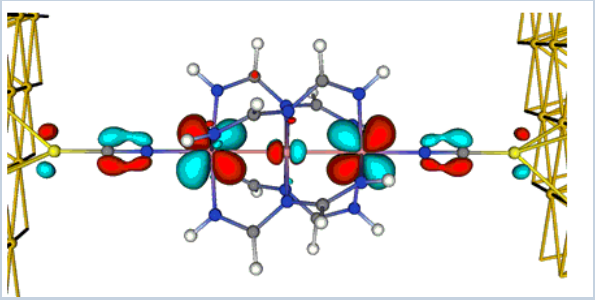


Co_3: zero bias transmission

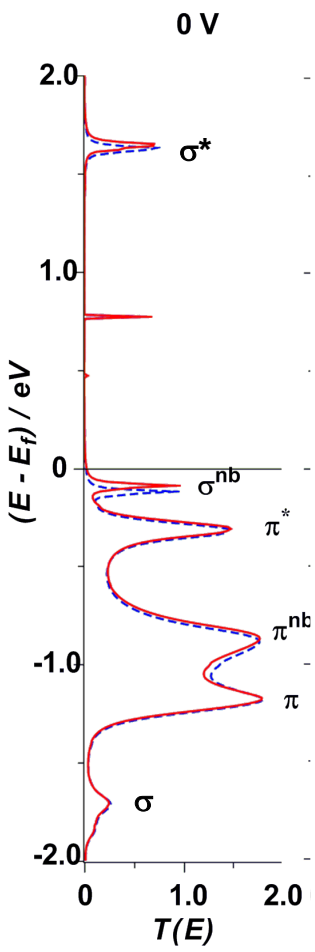


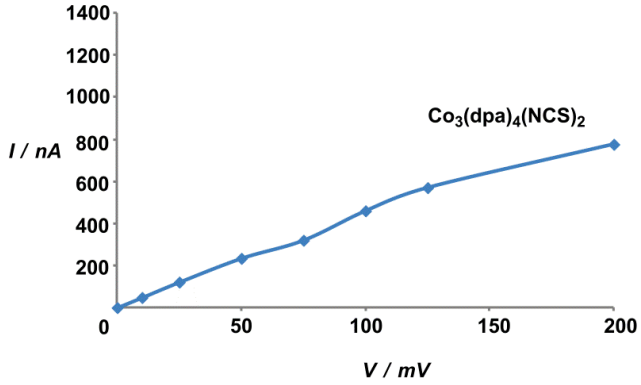




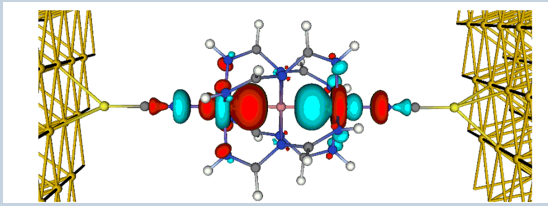


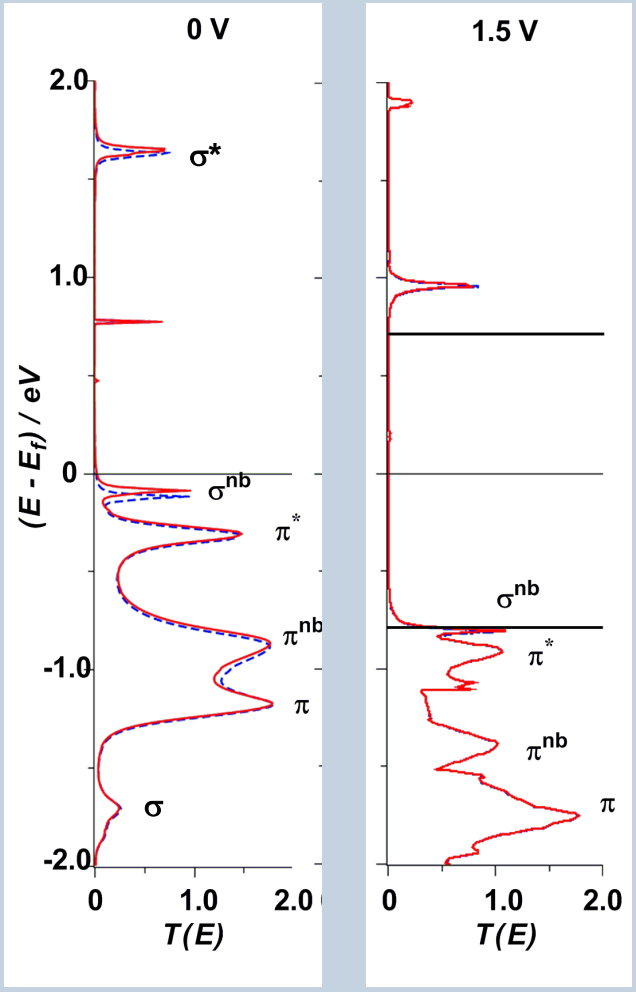
Co_3: finite bias transmission

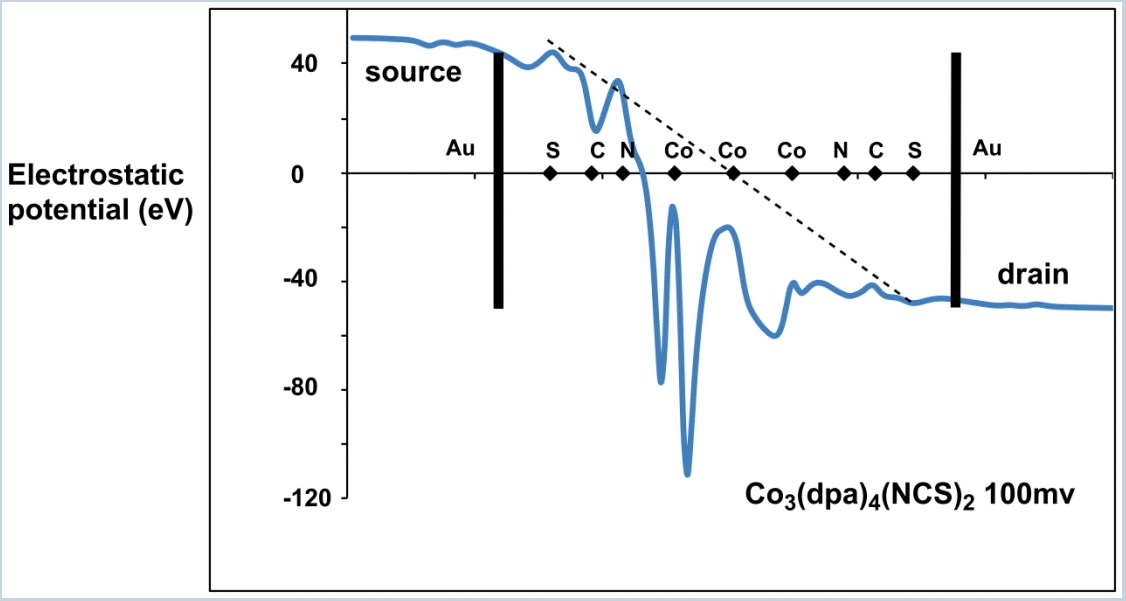




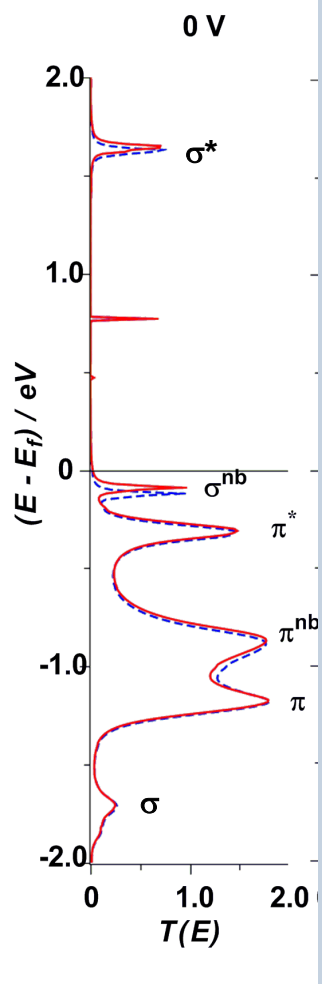
Co_3: finite bias transmission

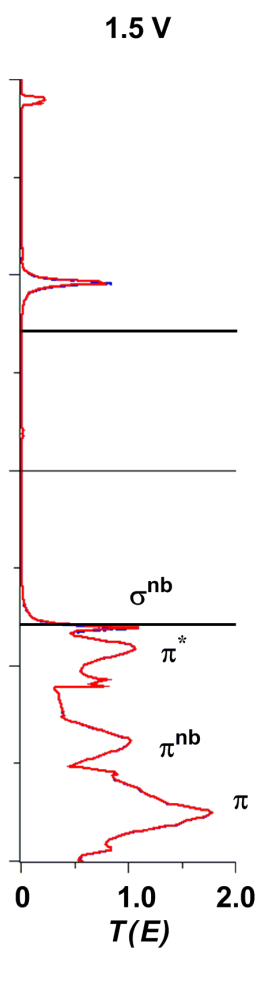


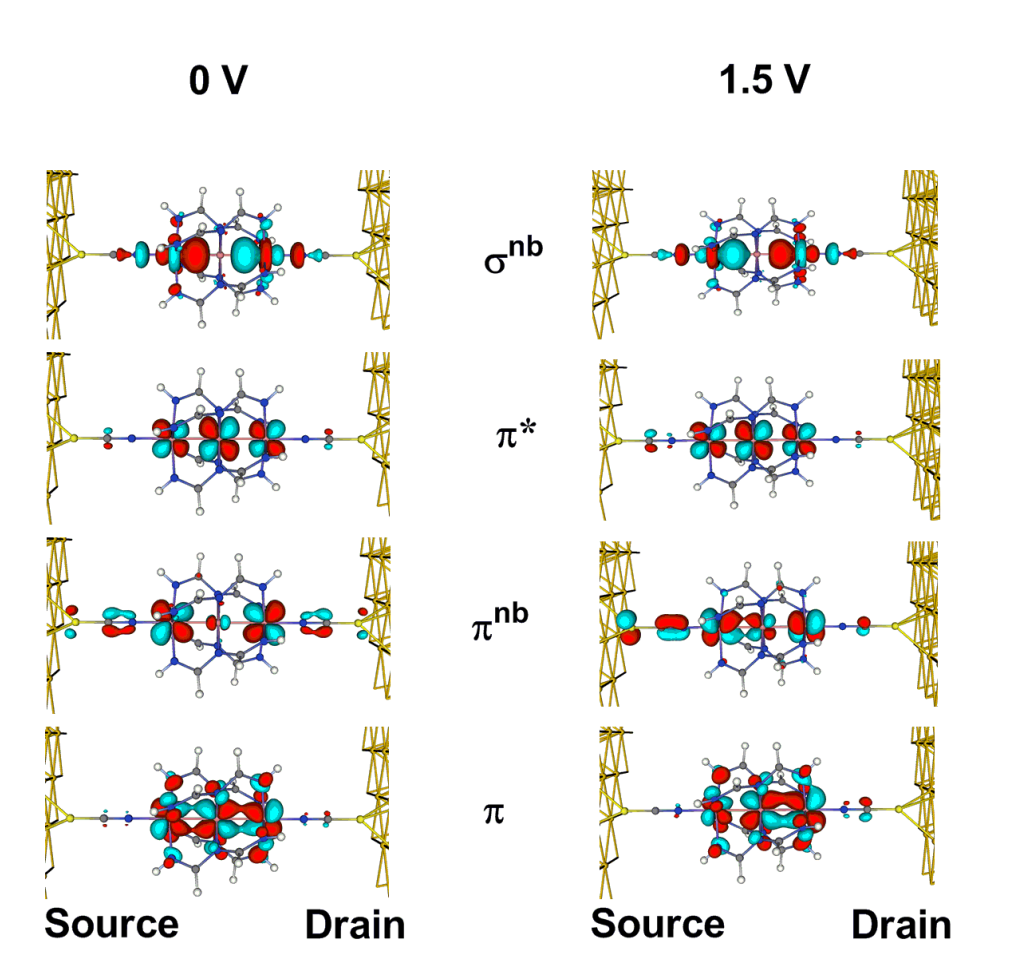




Co_3: finite bias transmission



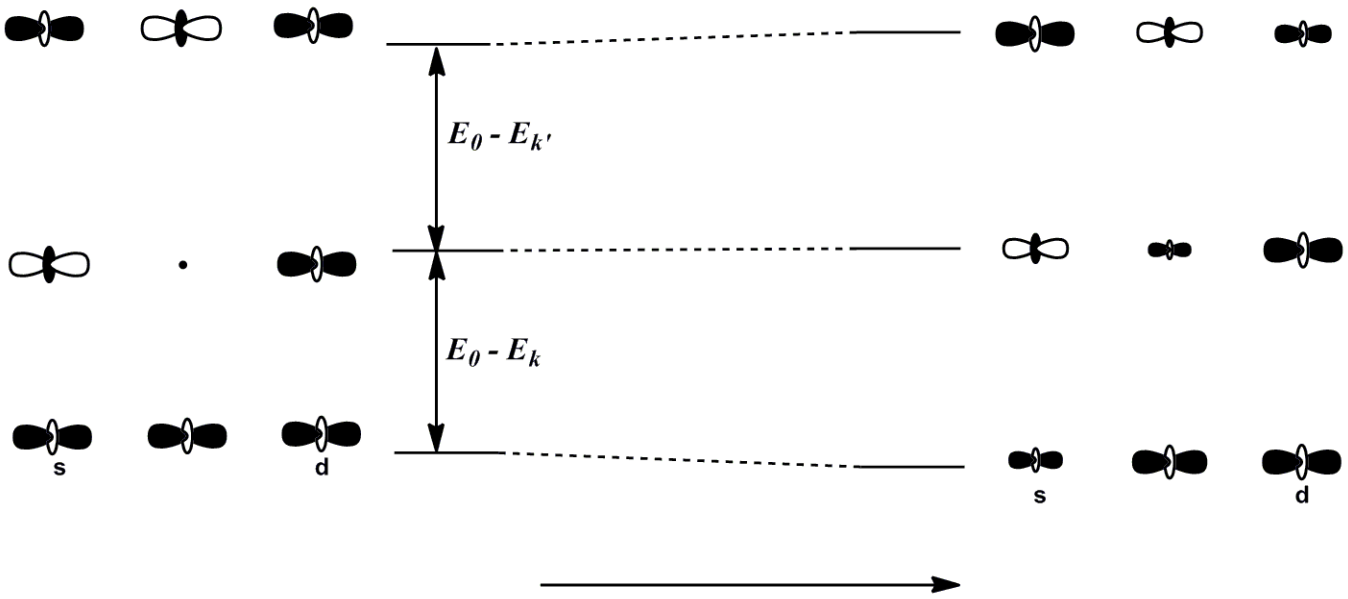




What is ‘delocalisation’?

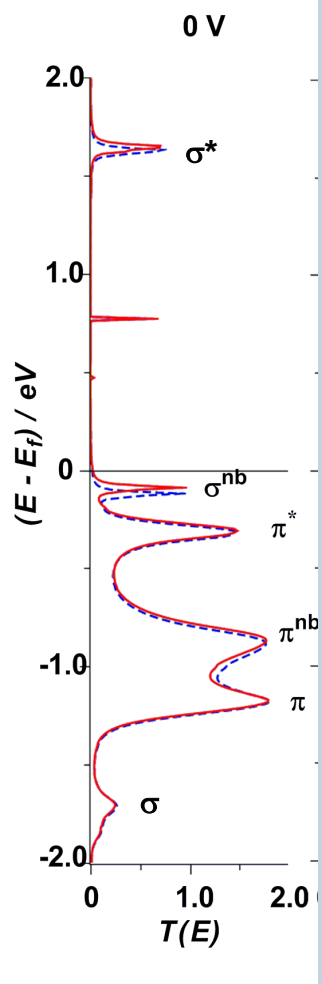
$$H^{(1)} = -\mu_z \varepsilon$$

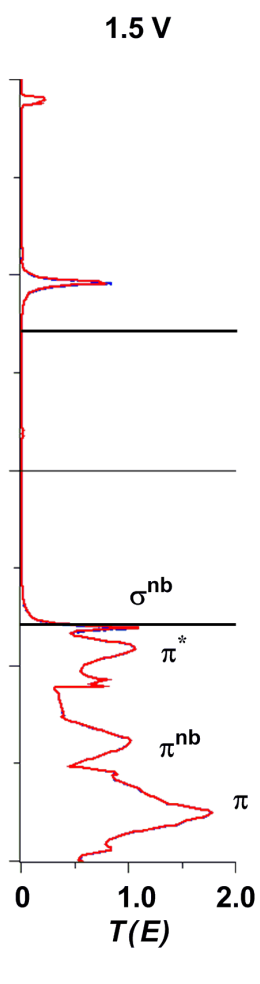
$$\psi \approx \psi_0 + \sum_k{}' \left\{ \frac{\langle \psi_k | H^{(1)} | \psi_0 \rangle}{E_0 - E_k} \right\} \psi_k$$

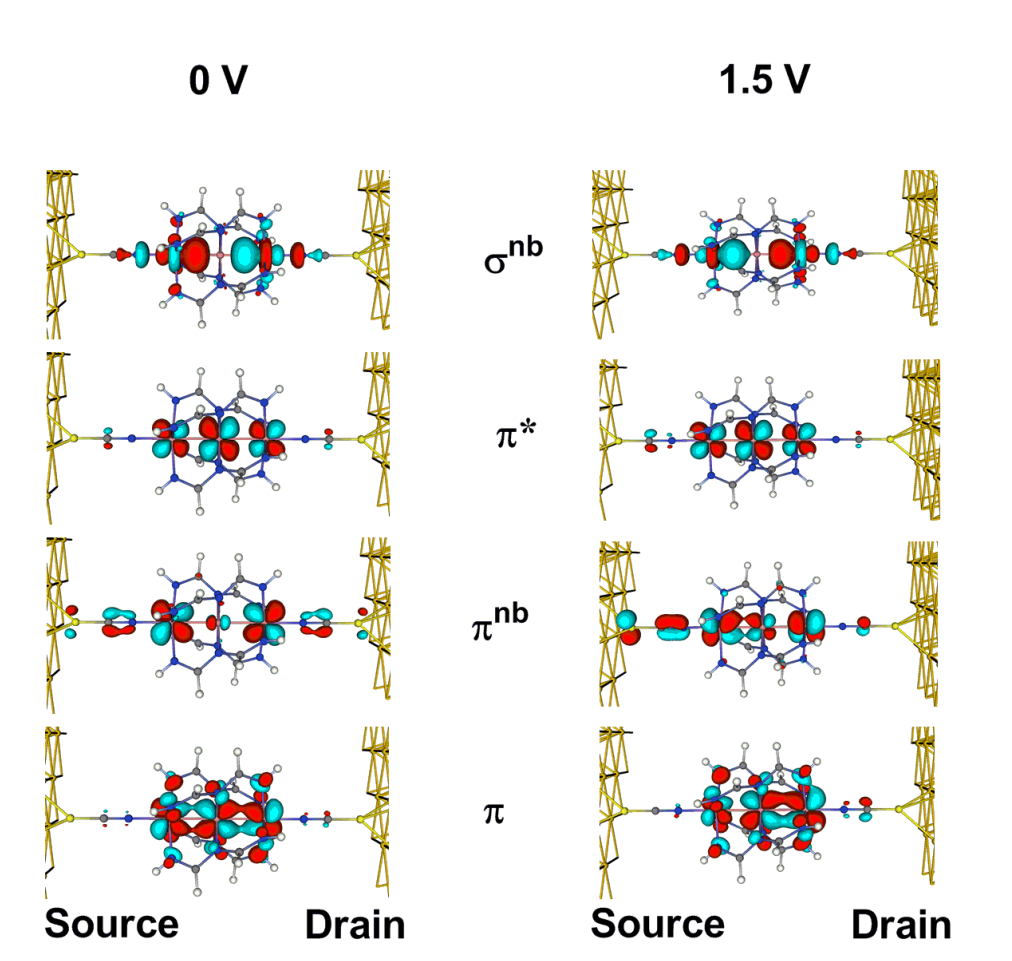


$$H^{(1)} = -\mu_z \varepsilon$$

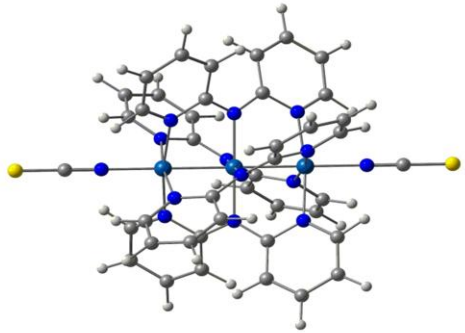
Co_3: finite bias transmission



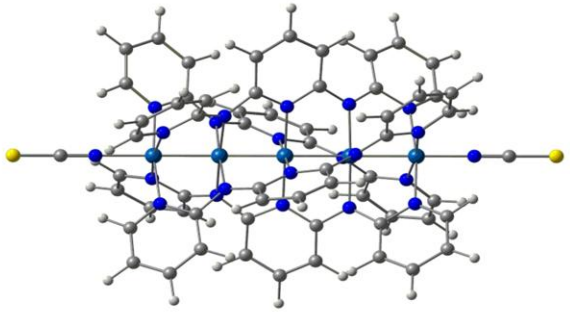




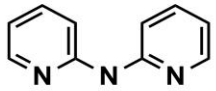
Chain length: Co_3 vs Co_5?



$Co_3(dpa)_4(NCS)_2$

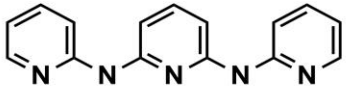


$Co_5(tpda)_4(NCS)_2$



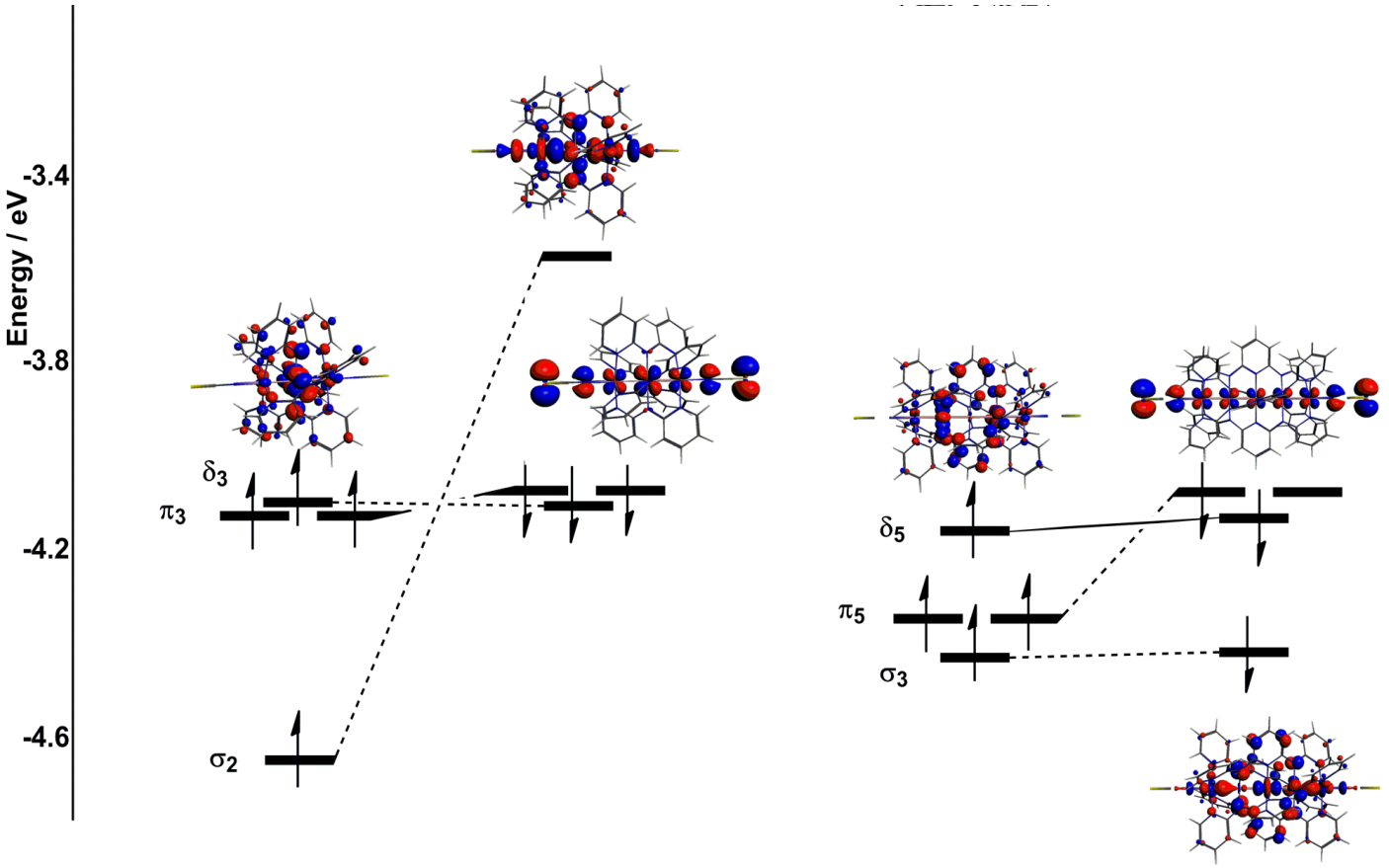
dpa

G* = 530 n*S



tpda

G* = 100 n*S



$Co_3(dpa)_4(NCS)_2$
$^2A_2$

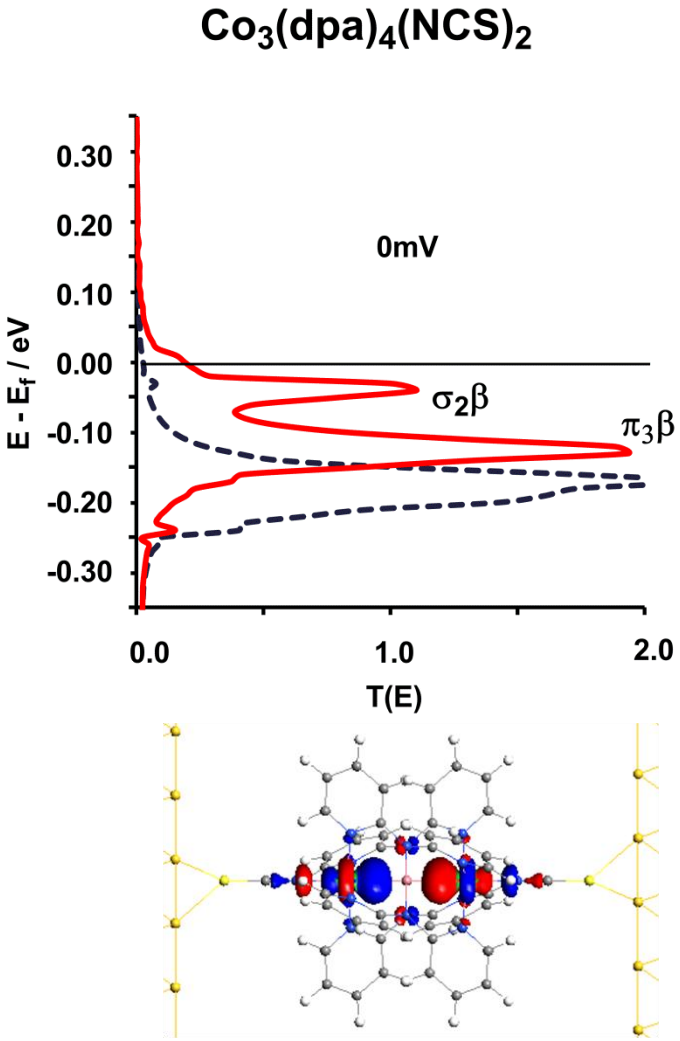
Co-Co = 2.32 Å

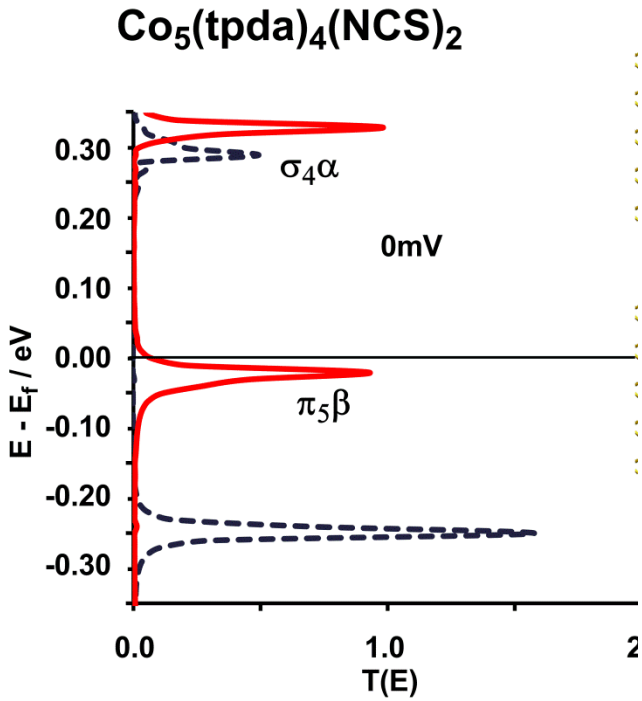
$\mu \approx \mu_{s.o.}$

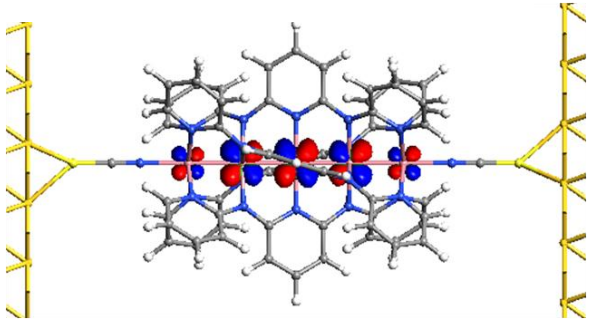
$Co_5(tpda)_4(NCS)_2$
^2E

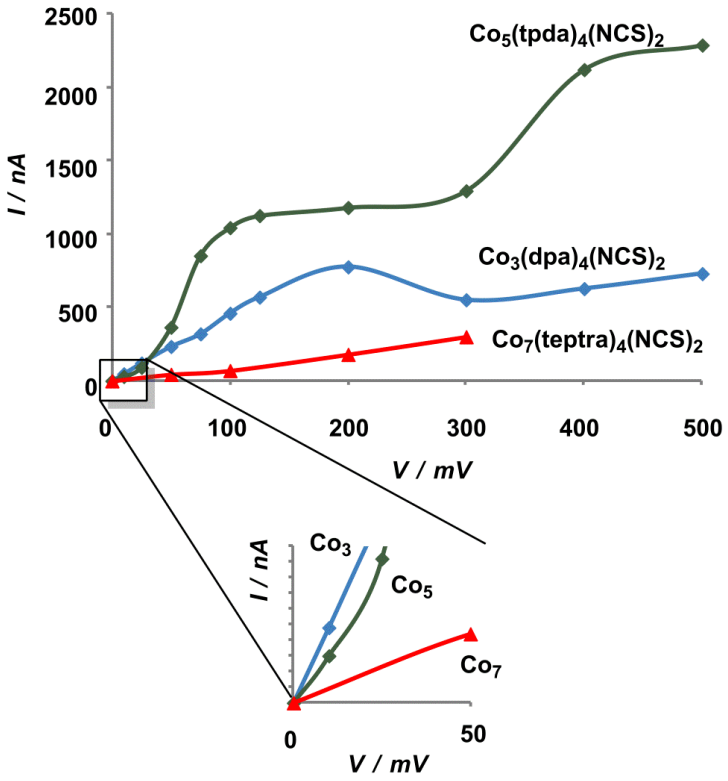
Co-Co = 2.25 Å

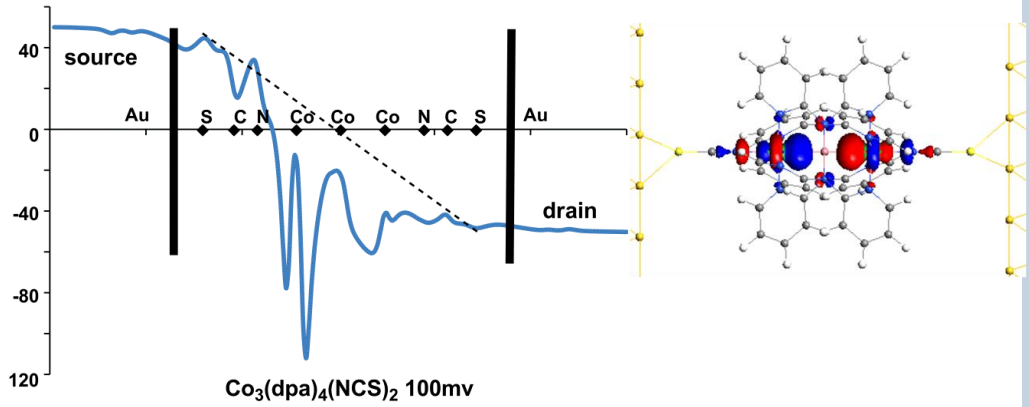
$\mu > \mu_{s.o.}$

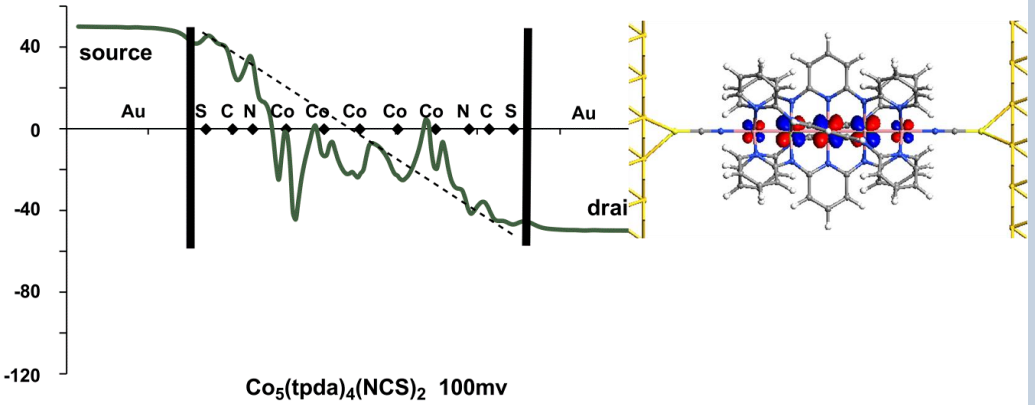

$Co_3(dpa)_4(NCS)_2$
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
E - E$_f$ / eV
0mV
$\sigma_2\beta$
$\pi_3\beta$
0.0
1.0
2.0
T(E)


$Co_5(tpda)_4(NCS)_2$
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
E - E$_f$ / eV
$\sigma_4\alpha$
0mV
$\pi_5\beta$
0.0
1.0
T(E)

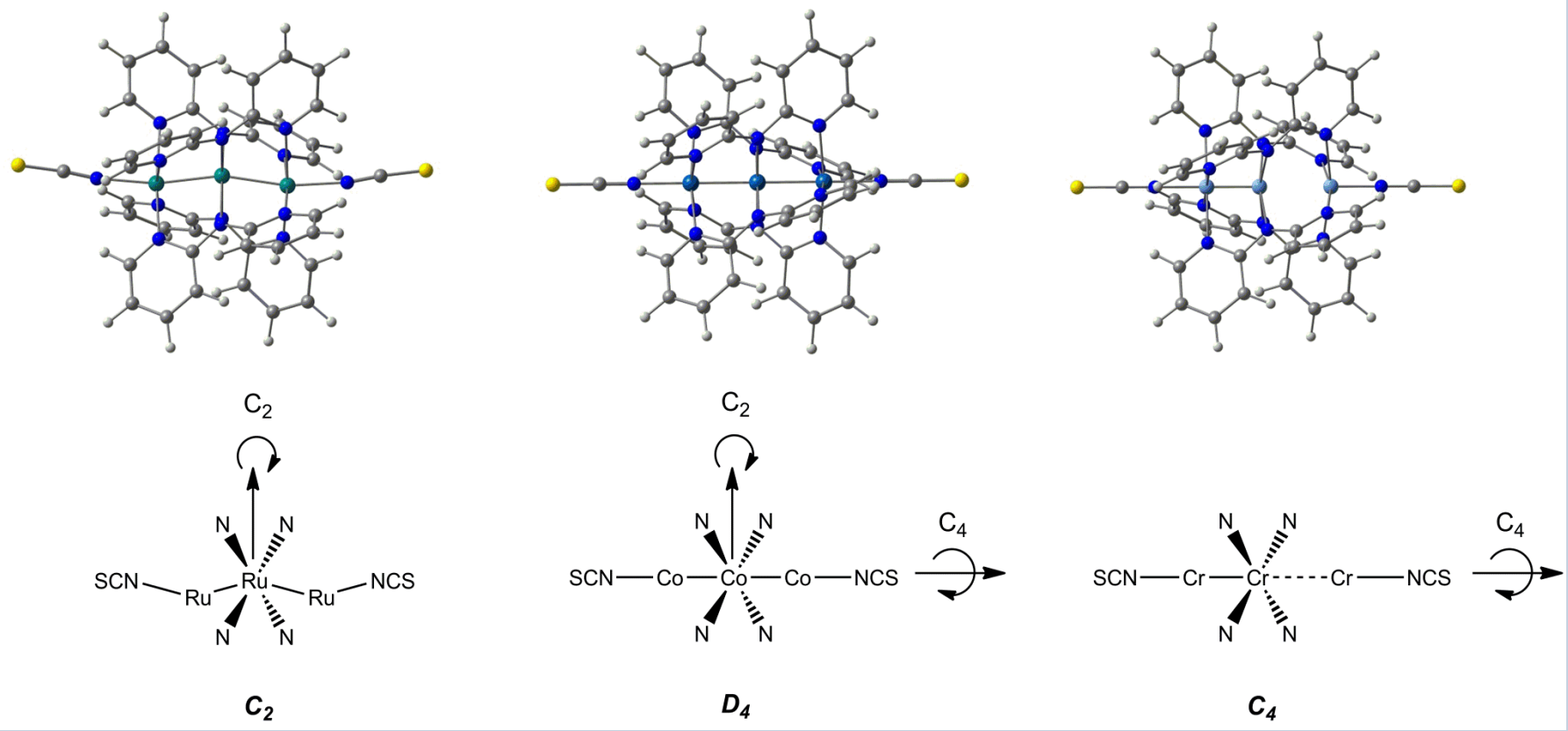



2500
2000
1500
1000
500
0
I / nA
Co5(tpda)4(NCS)2
Co3(dpa)4(NCS)2
Co7(teptra)4(NCS)2
0
100
200
300
400
500
V / mV
Co3
Co5
Co7
I / nA
0
50
V / mV

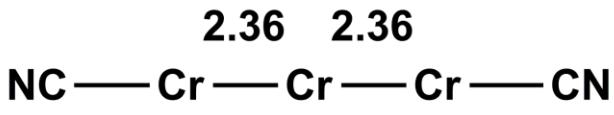

40
0
-40
-80
120
source
Au
S C N Co Co Co N C S
Au
drain
Co3(dpa)4(NCS)2 100mv

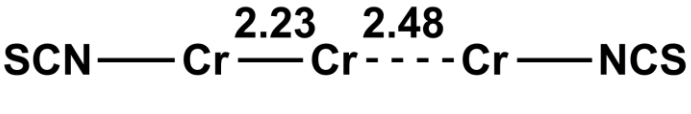

40
0
-40
-80
-120
source
Au
S C N Co Co Co Co Co N C S
Au
drai
Co5(tpda)4(NCS)2 100mv

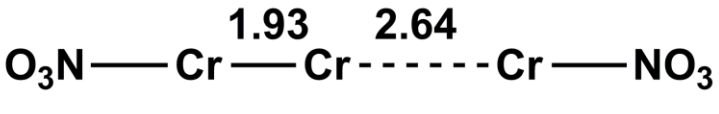
Bends and breaks



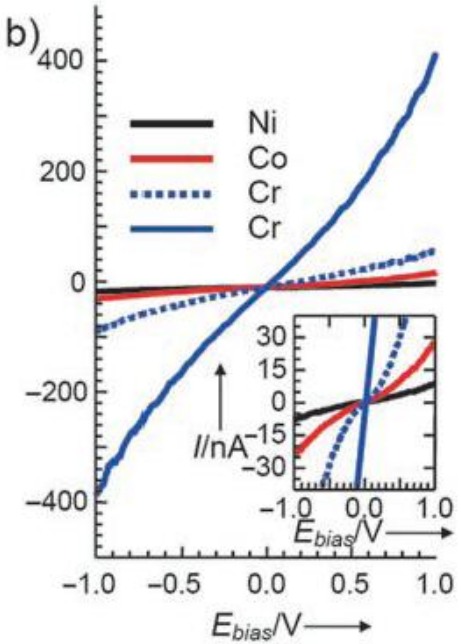
Structural diversity in Cr_3 EMACs

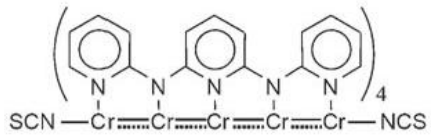




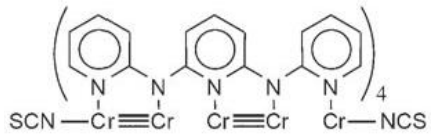


(*S* = 2 in all cases)





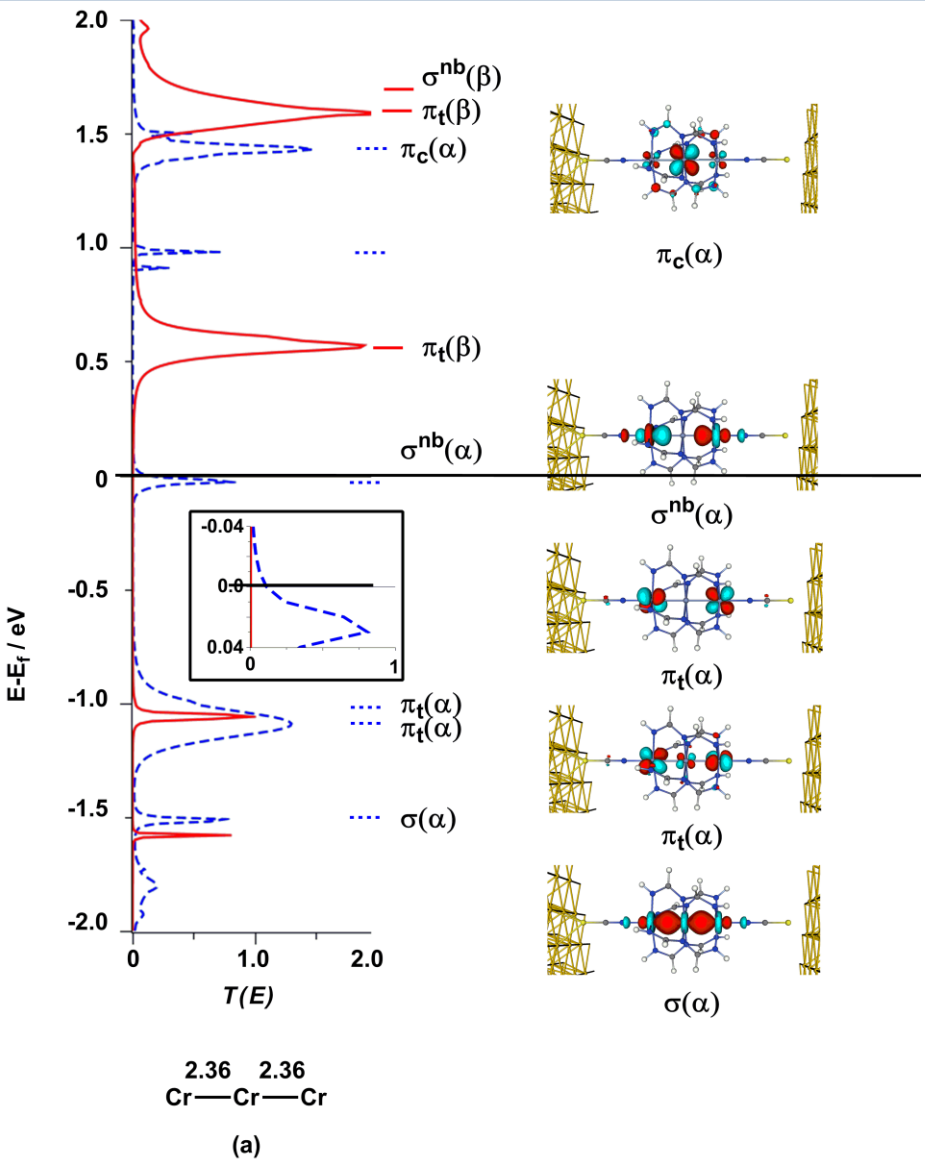
f)



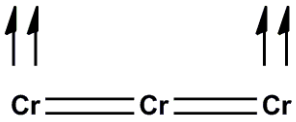
Co_3 vs Cr_3

G/μ*S*	STM	c-AFM	DFT
Cr	1.11	0.37	4.48
Co	0.53	0.021	0.42

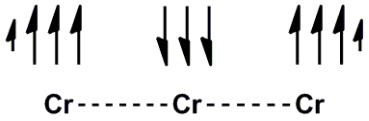
$$\frac{G(Cr_3)}{G(Co_3)}$$: c-AFM (17.6) > DFT (10.6) > STM (2.1)



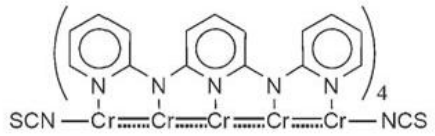
(a)



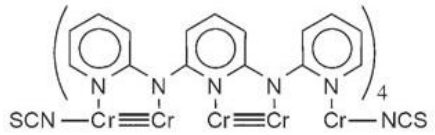
incorrect!

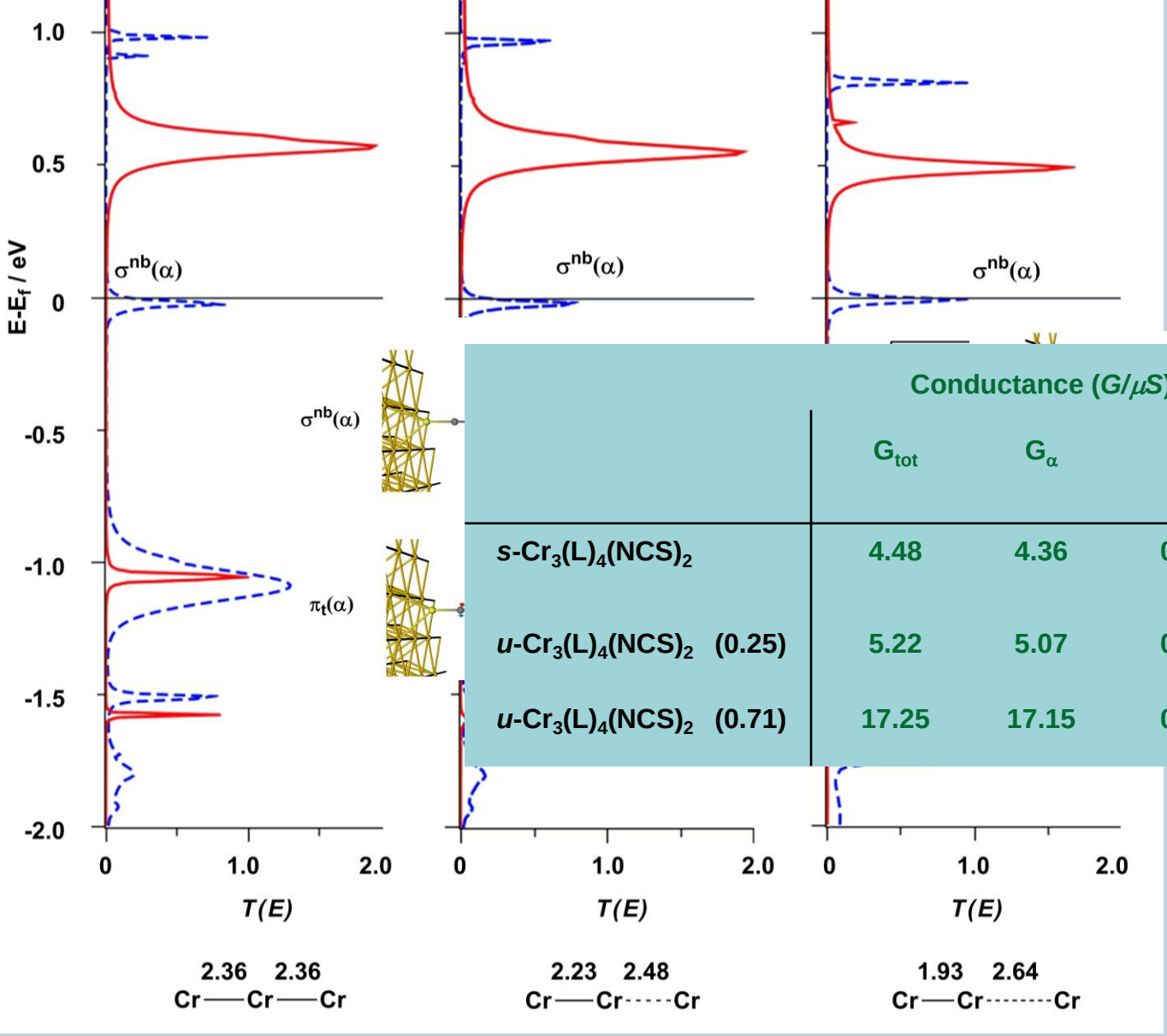


more accurate!



f)





	Conductance ($G/\mu S$)		
	G_{tot}	G_α	G_β
s-$Cr_3(L)_4(NCS)_2$	4.48	4.36	0.12
u-$Cr_3(L)_4(NCS)_2$ (0.25)	5.22	5.07	0.15
u-$Cr_3(L)_4(NCS)_2$ (0.71)	17.25	17.15	0.10

Conclusions

Structure/function relationships are subtle and often counterintuitive: (first row) transition metal ions are not the same as carbon!

Conductance can actually *increase* with chain length in metal-atom chains

Low-symmetry distortions can *increase* conductance

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