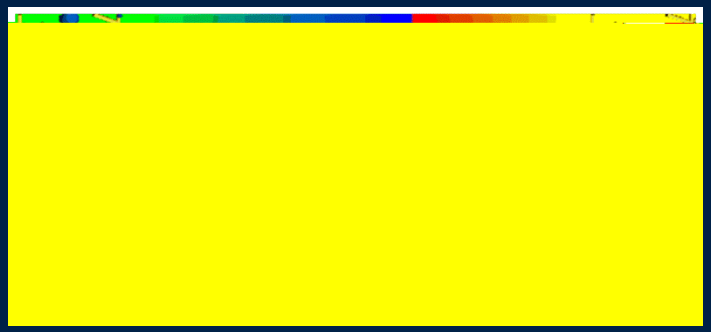
Inorganic Chemistry Laboratory,
Department of Chemistry,
University of Oxford

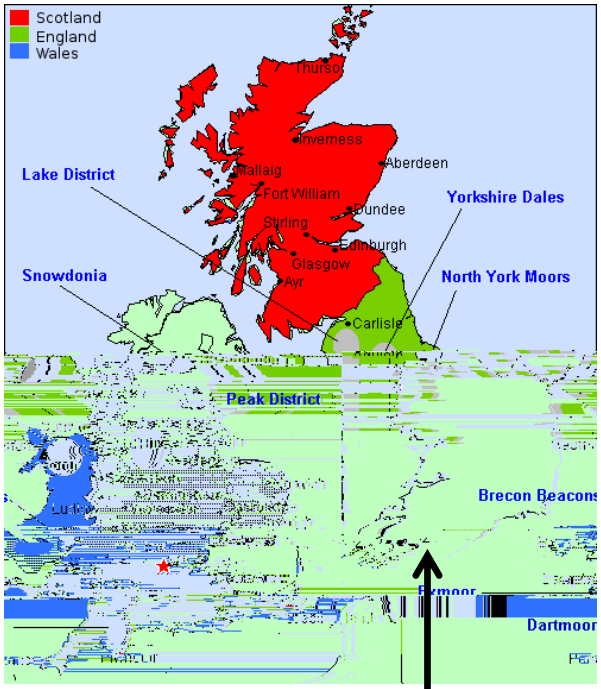
UNIVERSITY OF OXFORD

Molecular Wires: from metal-metal bonds to electron transport



John McGrady, University of Oxford

March 14, 2013 Peking University, Beijing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England
Wales
Thurso
Inverness
Aberdeen
Lake District
Mallaig
Fort William
Yorkshire Dales
Dundee
Stirling
Edinburgh
Glasgow
Ayr
Snowdonia
North York Moors
Carlisle
Peak District
Brecon Beacons
Dartmoor

Oxford


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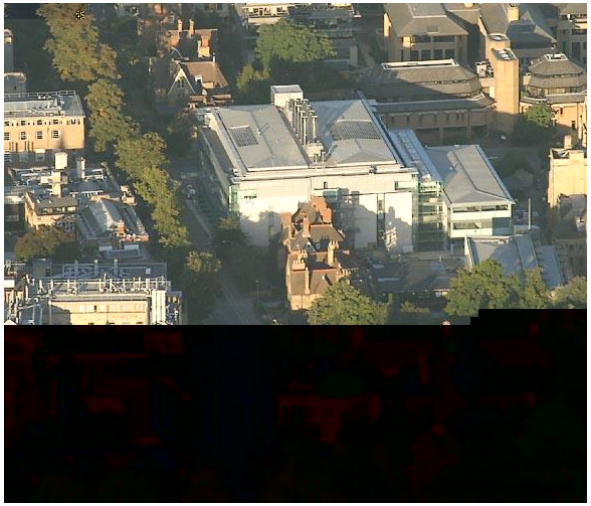
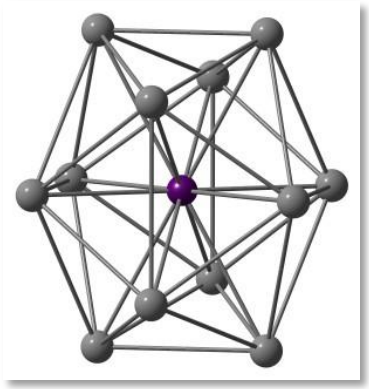


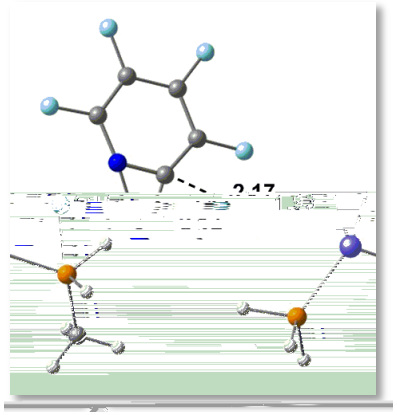
New College (founded 1379)

Computational Inorganic Chemistry

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

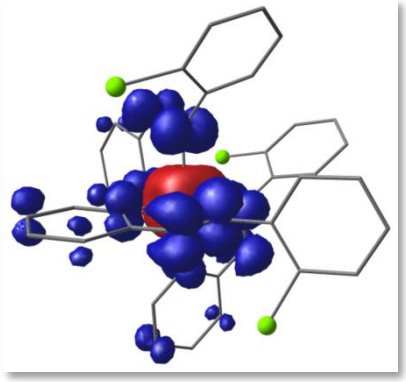


Organometallic reaction mechanisms

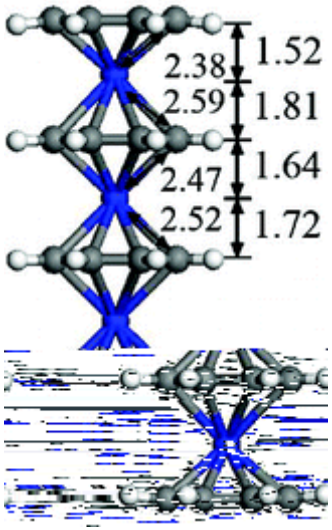


Molecular electronics

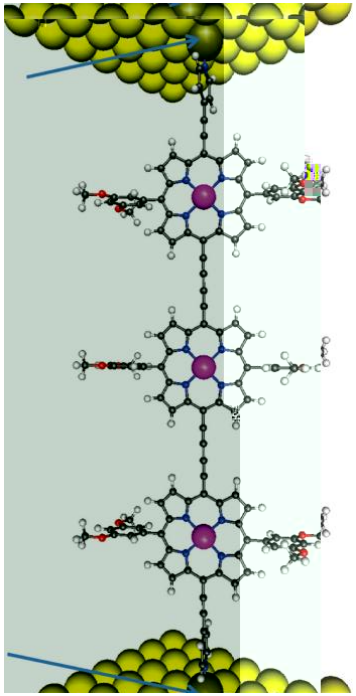
Non-innocent ligands



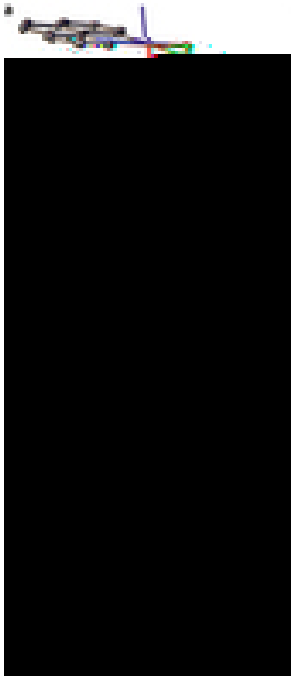
‘Molecular wires’



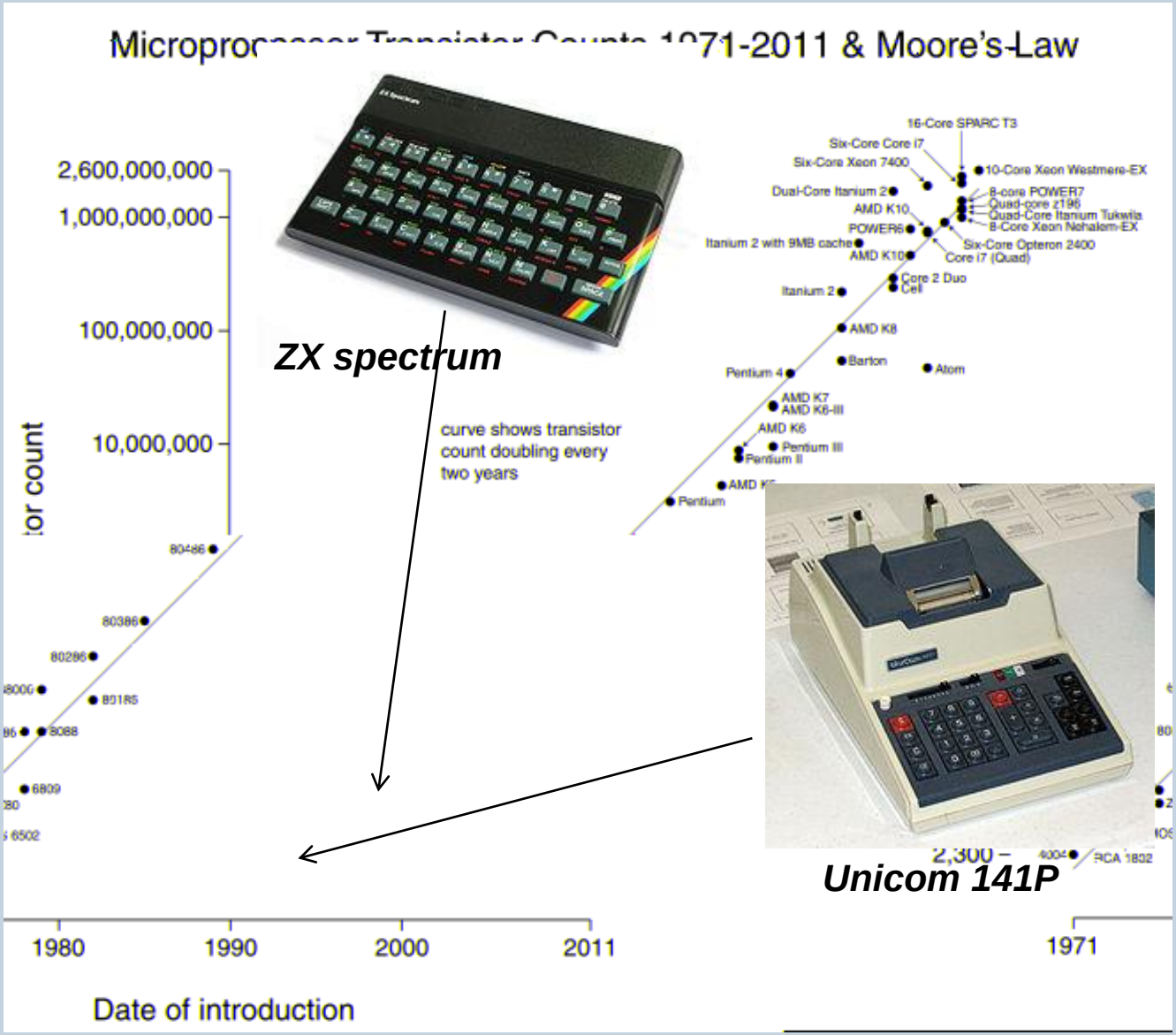
Fe COT derivatives:
Huang, Li *et al*.,
***J. Phys. Chem*., 2010.**

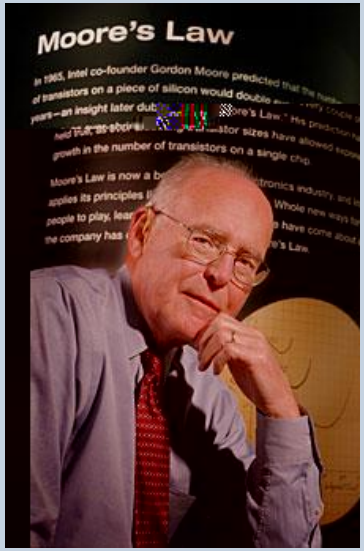


Zn porphyrins:
Anderson *et al*.,
***Nat. Nanotech.*, 2011.**

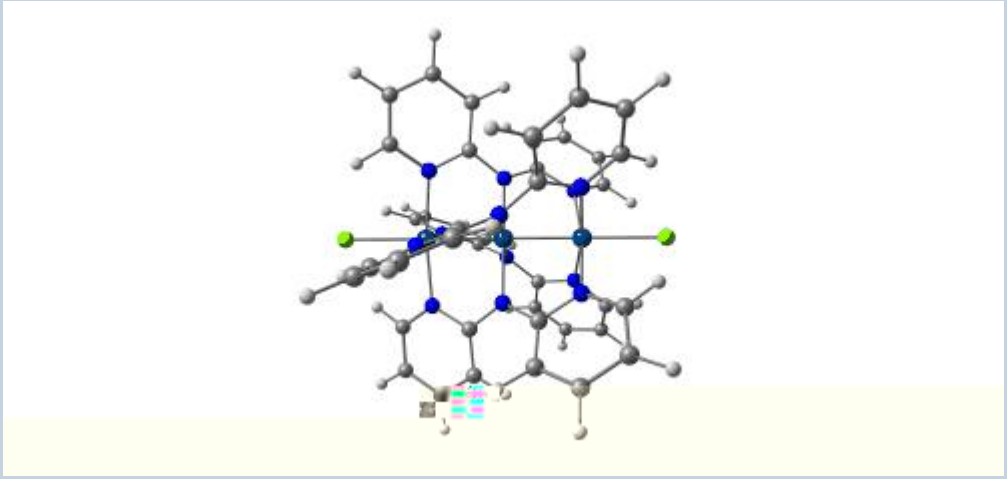


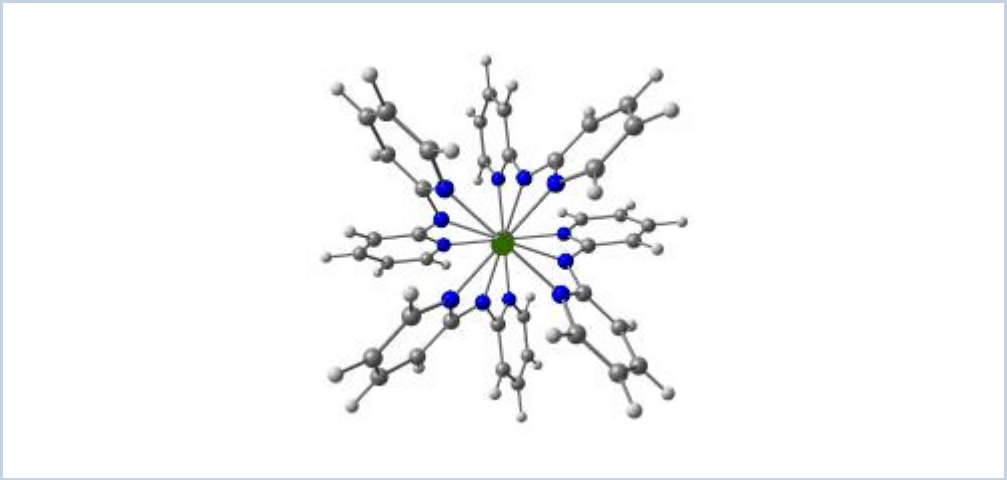
$(Pd^{2.5+})_{\sim 1000}$
Ritter,
***Nat. Chem*. 2011**


Microprocessor Transistor Counts 1971-2011 & Moore's Law
2,600,000,000
1,000,000,000
100,000,000
10,000,000
ZX spectrum
curve shows transistor count doubling every two years
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
8088
6809
6502
2,300
4004
RCA 1802
Unicom 141P
1980
1990
2000
2011
1971
Date of introduction


Moore's Law

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





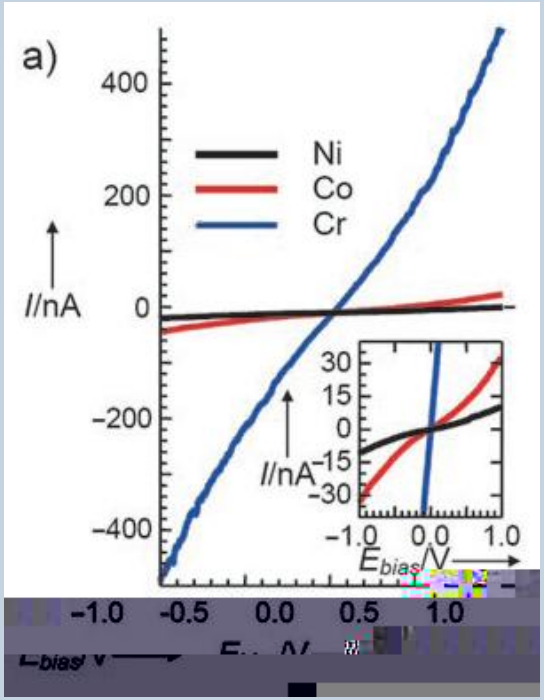
Homotrimetallic: 1st row
Cr_3, Co_3, Ni_3, Cu_3

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

Experiments: trimetallic chains

STM

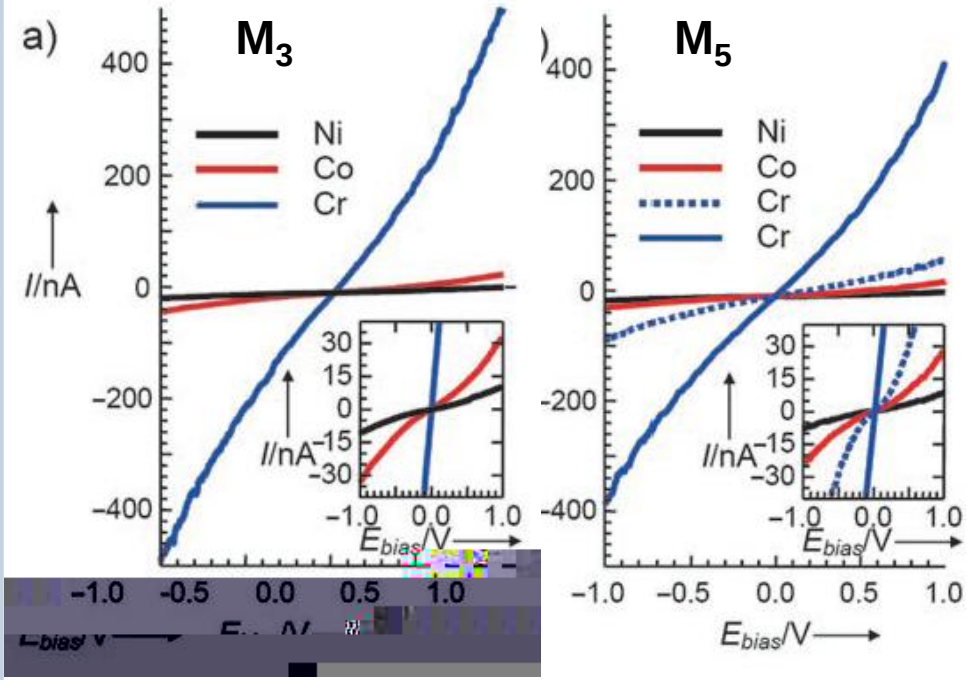


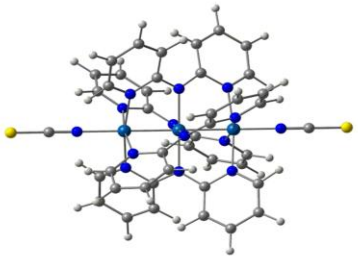
G/n*S*	STM	c-AFM
Cr_3	1110	370
Co_3	530	21
Ni_3	290	5.8
Ru_3	760	

$$G \quad \frac{1}{R} \quad \frac{I}{V}$$

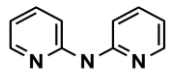
Peng, Chen *J. Phys. Chem. B* 2004, *108*, 959,
Angew. Chem. Int. Ed. 2006, *45*, 5814,
Chem Comm., 2010, *46*, 1338.

M_3 vs M_5 chains



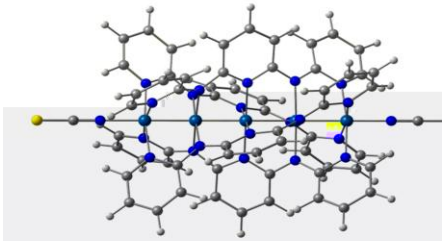


$Co_3(dpa)_4(NCS)_2$

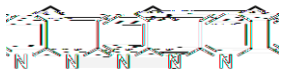


dpa

***G* = 530 nS**



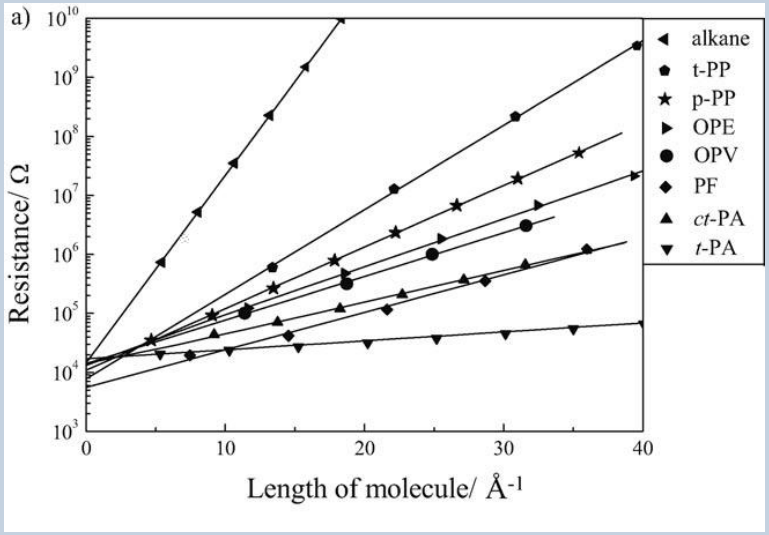
$Co_5(tpda)_4(NCS)_2$

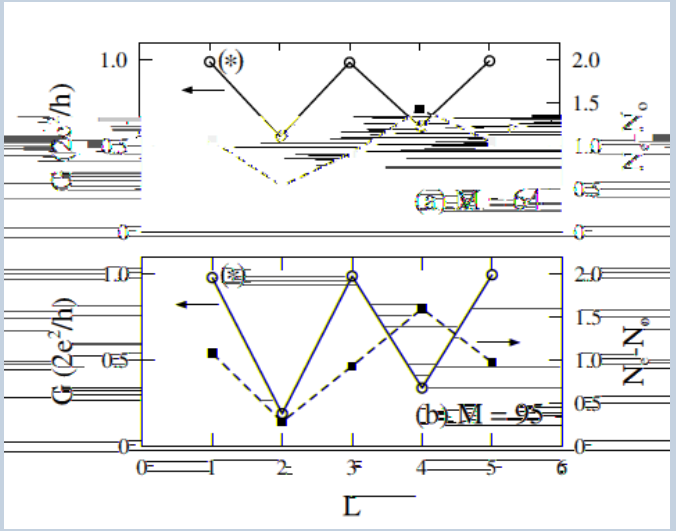


tpda

***G* = 100 nS**

Models for length dependence:





Exponential decay:

$$R \quad R_c e^{\quad r}$$

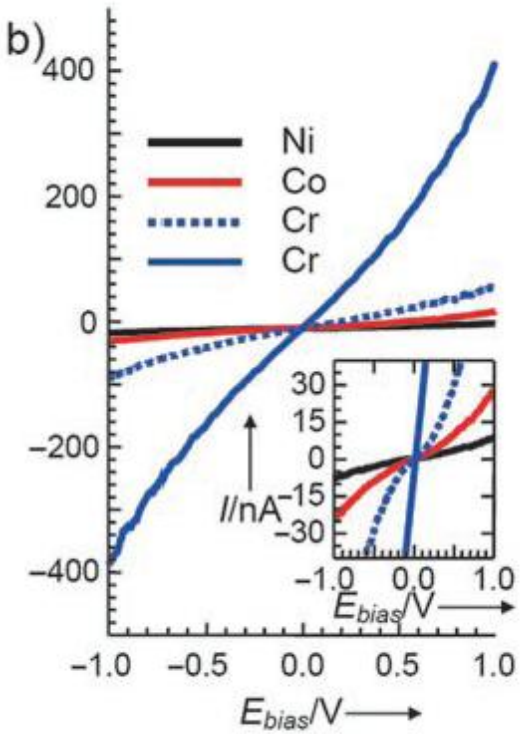
Zhao, *ChemPhysChem*, 2008.

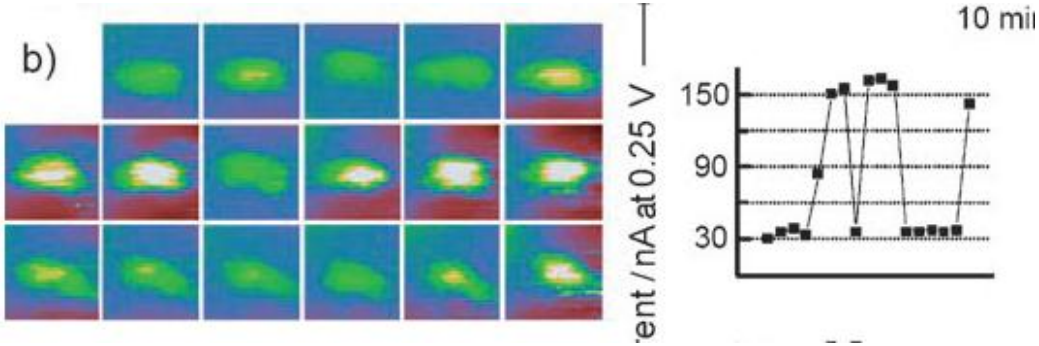
$(Co_{3/5}) = 0.2$ Å^{-1}

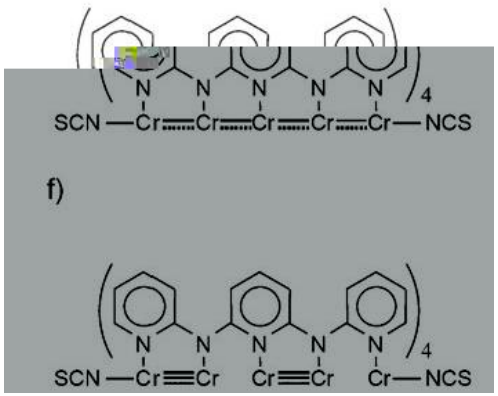
Odd-even oscillations in Na_x:

Sim, *PRL*, 2001.

M_5 chains







'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 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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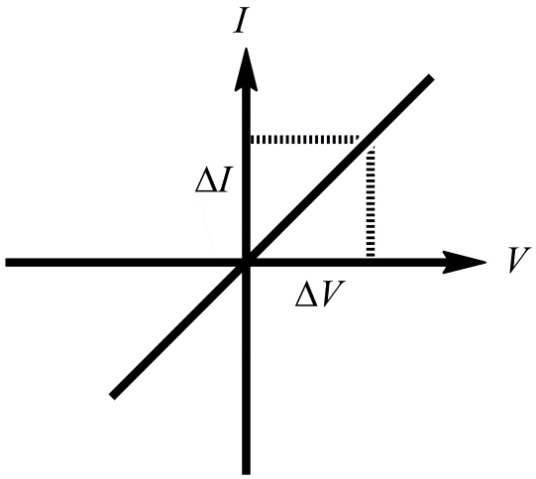
Current flow in macroscopic and nanoscale conductors:

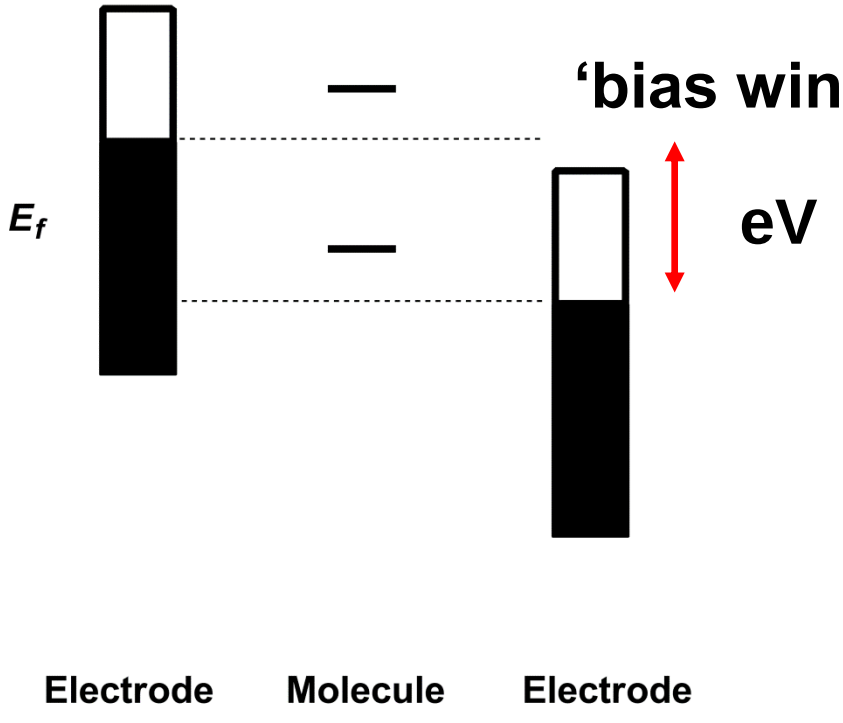


Ohm's law:

$$V \quad I$$

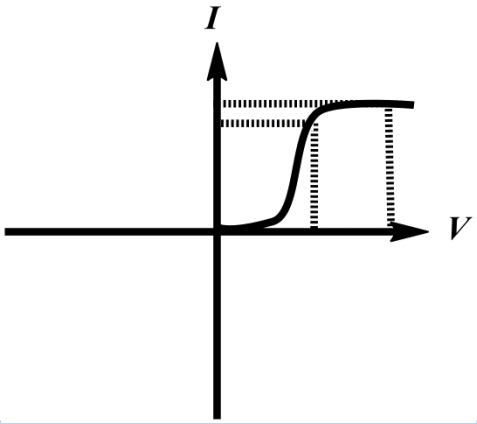
$$R \quad \frac{V}{I} \qquad G \quad \frac{1}{R} \quad \frac{I}{V}$$

Current flow in macroscopic and nanoscale conductors:



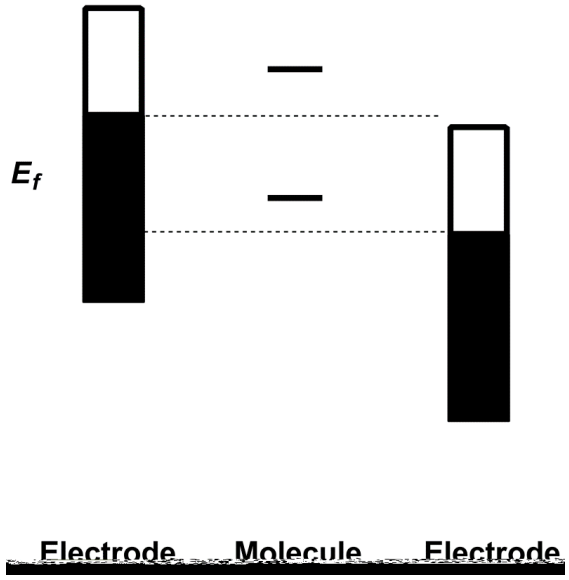
$$G_0 \quad 77nS$$

(quantum of conductance)

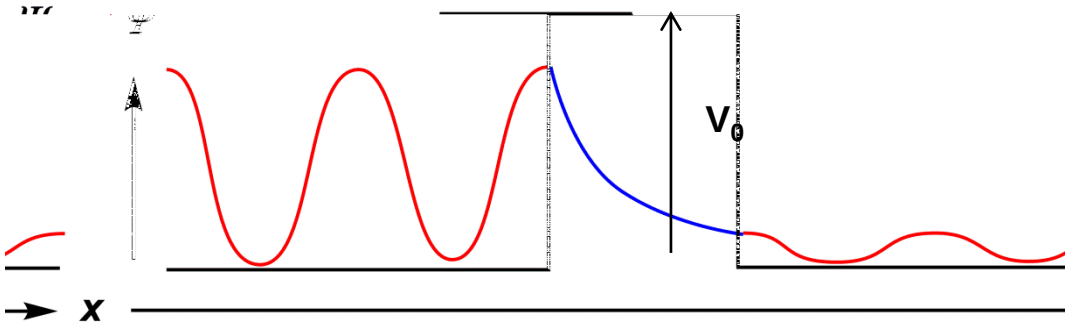


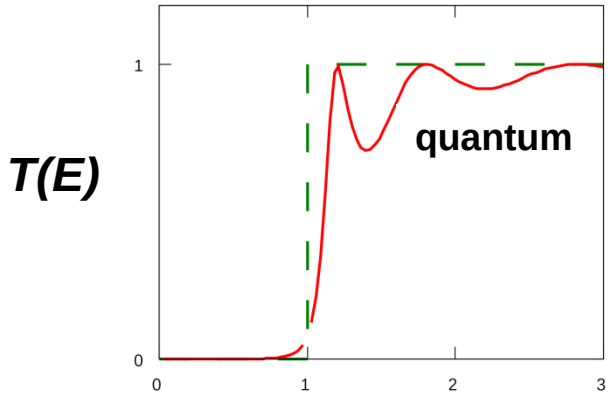
at finite T

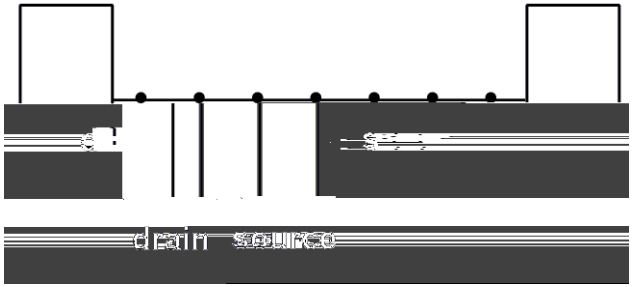
$$I(V, \ ) \quad \frac{e}{h} \quad \underbrace{T(E,V)}_{\text{transparency}} \quad \underbrace{f_L(E,V) \quad f_R(E,V)}_{\text{driving force}} \ dV$$



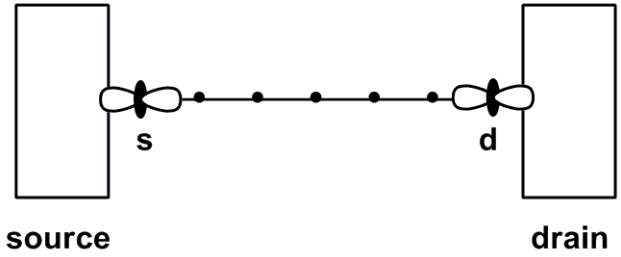
Transmission:



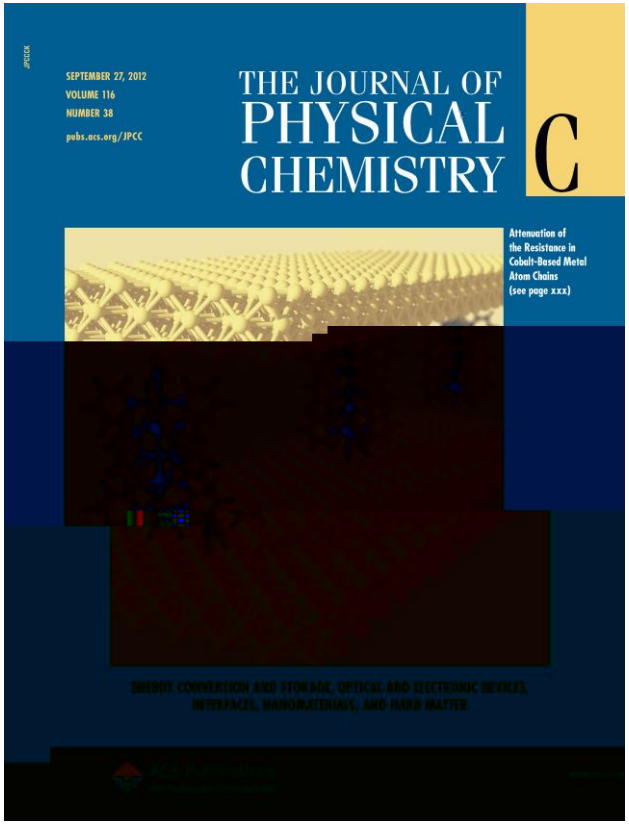




$$T(E) \quad \frac{4^{2} C_s^{2} C_d^{2}}{E^{2} {}^{2} C_s^{2} C_d^{2}}$$

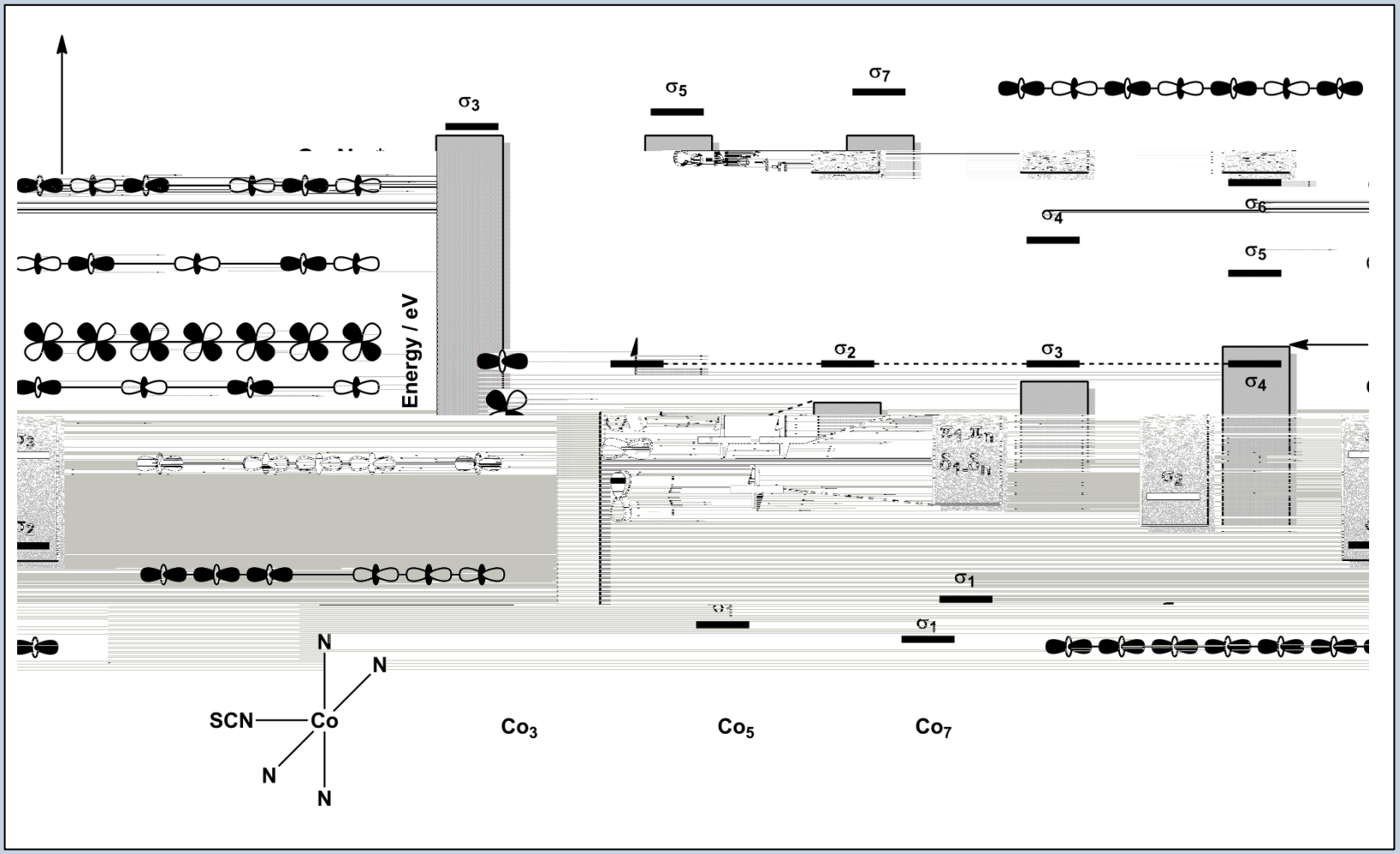


Methodology:

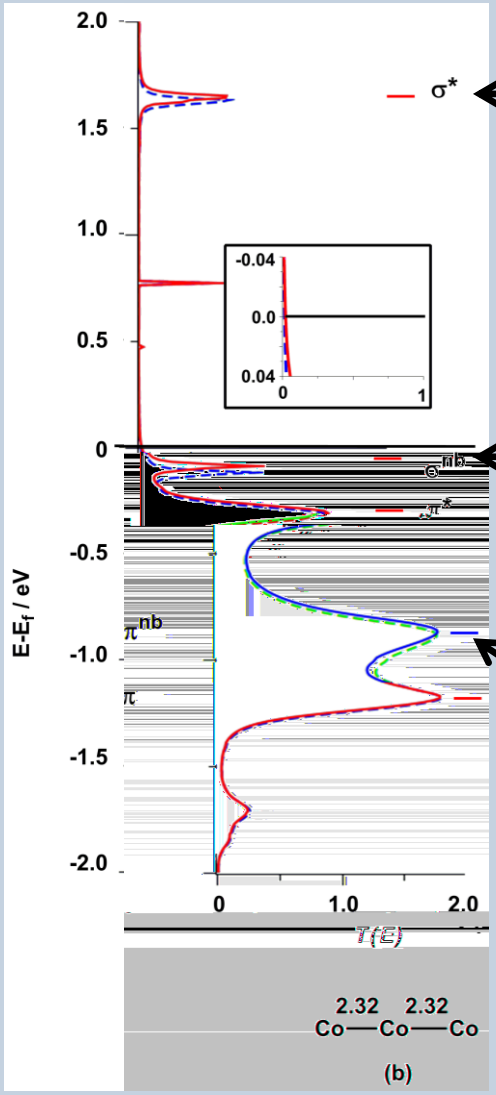


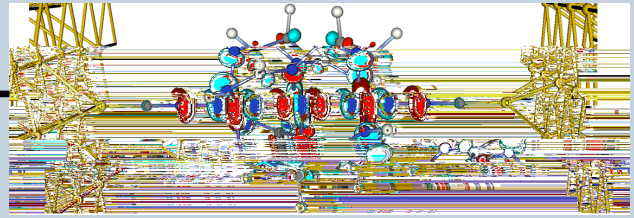
Transport calculations (LSDA+PZ): ATK2008/2010/2011 (NEGF)
Periodic boundary conditions perpendicular to transport direction (SIESTA)

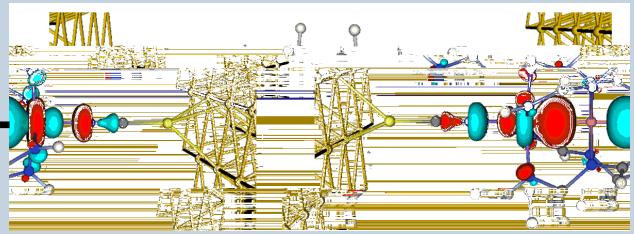
Co_n chains: 'the fruitfly' for transport calculations

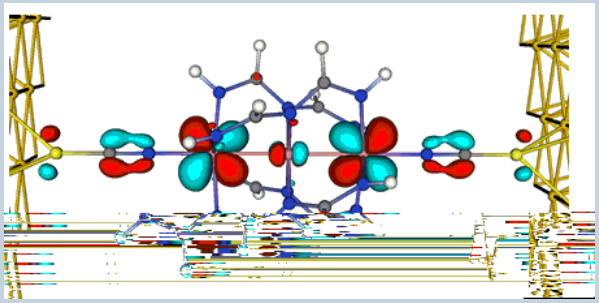


Co_3: zero bias transmission

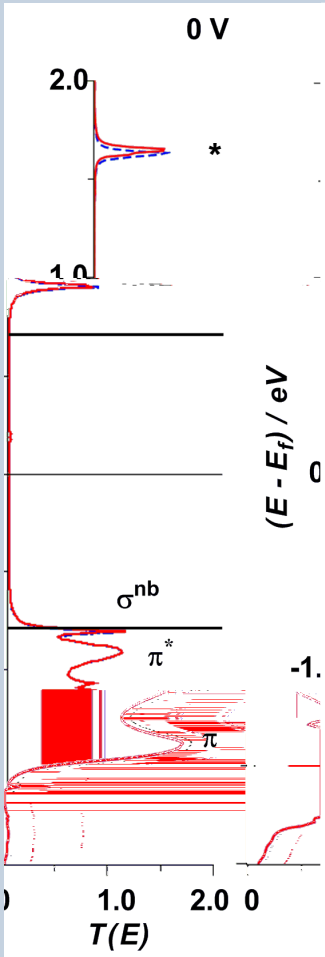


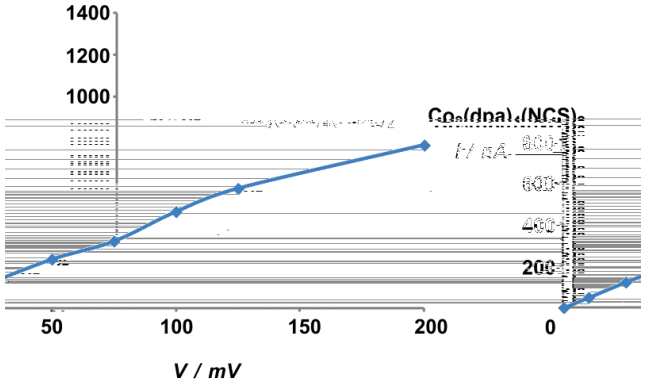




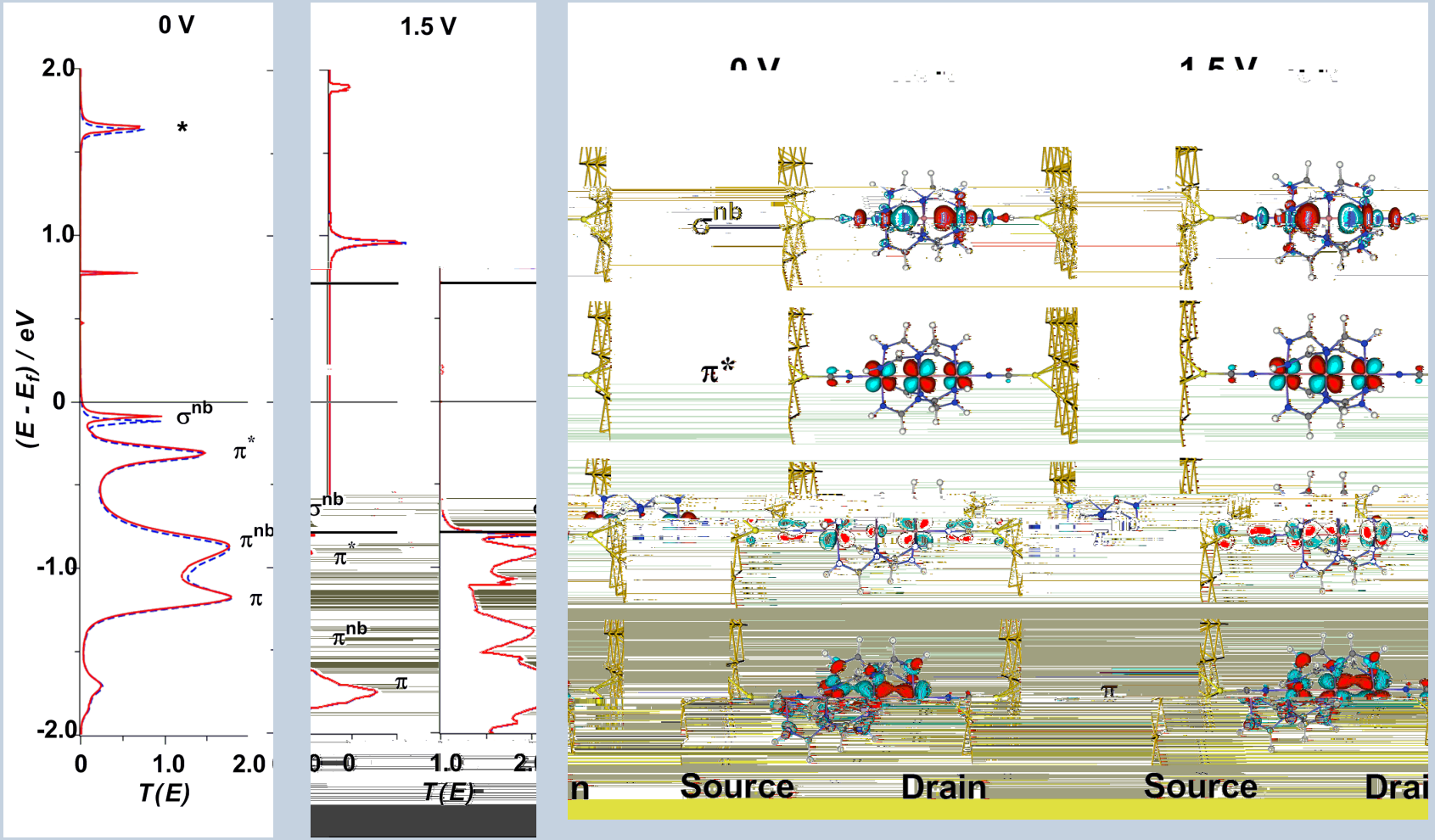


Co_3: finite bias transmission





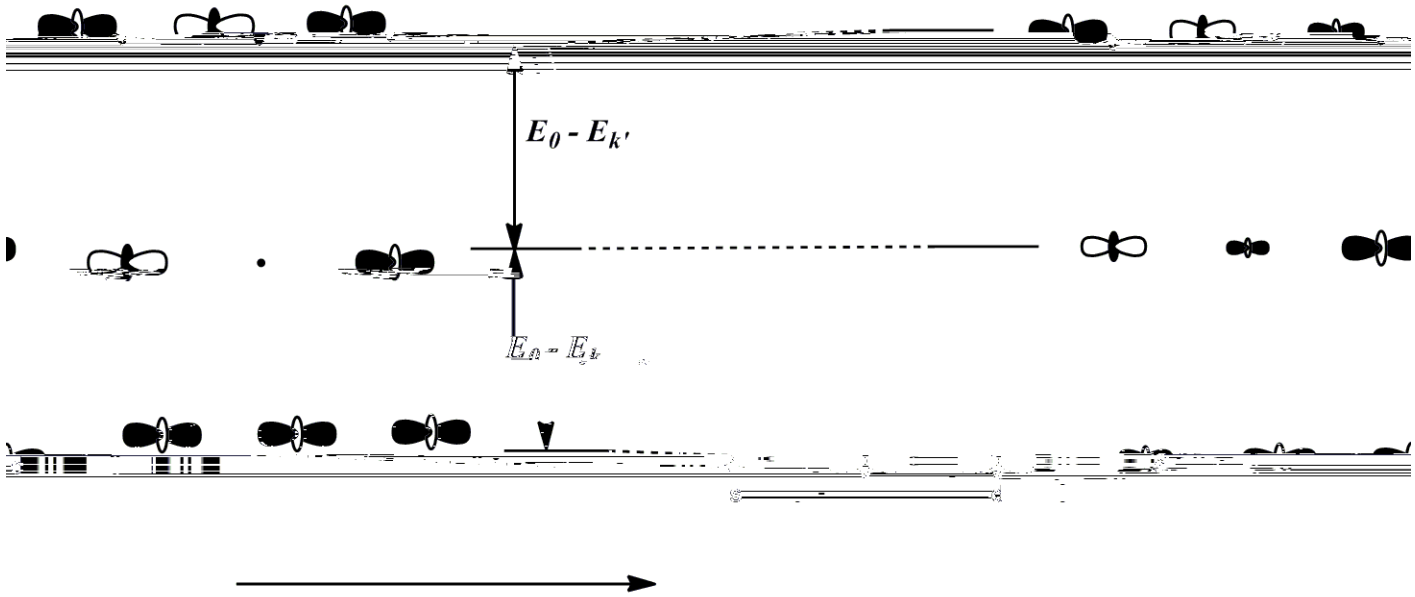
Co_3: finite bias transmission



What is ‘delocalisation’?

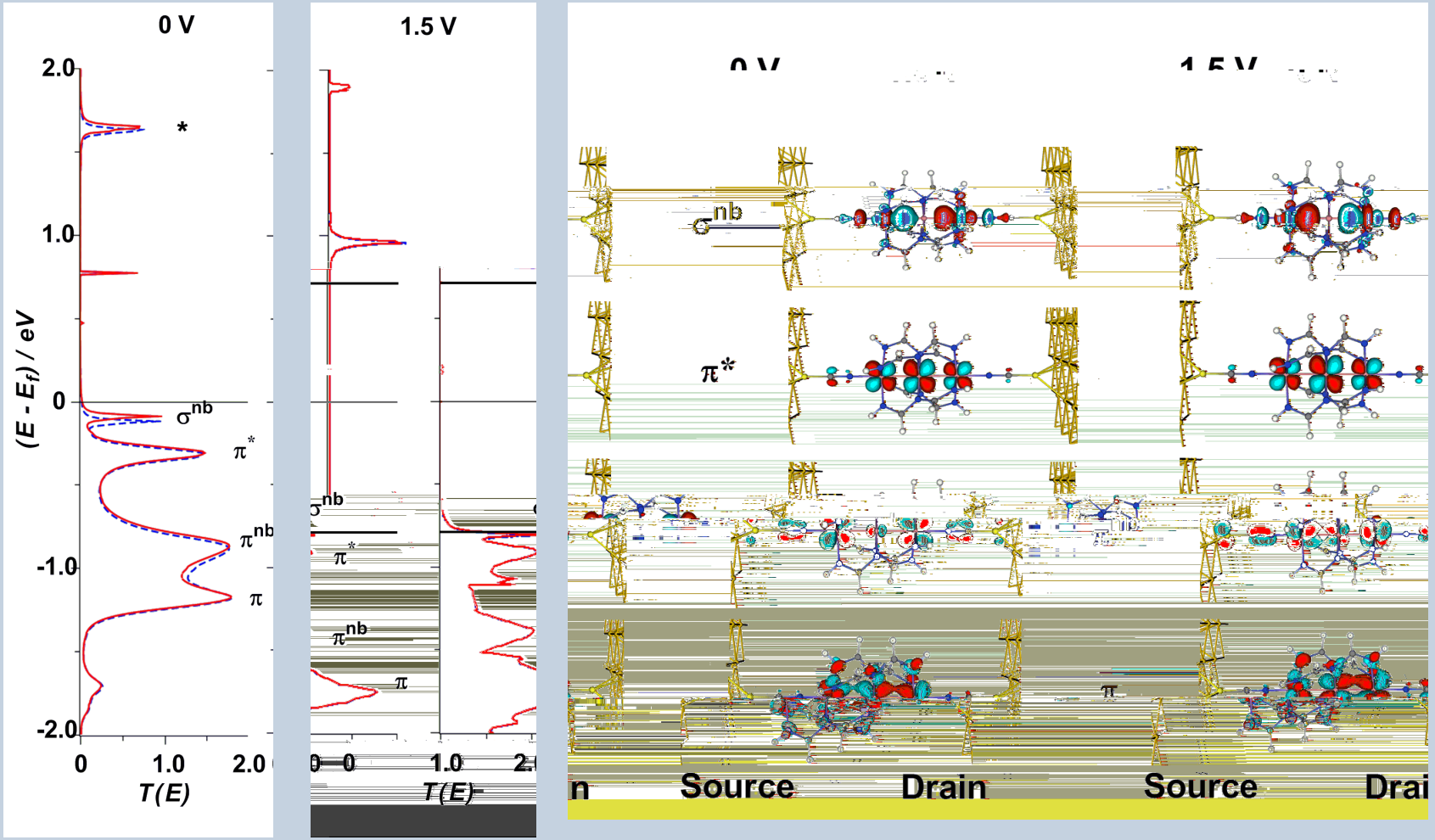
$$H^{(1)} = -\mu_z \varepsilon$$

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

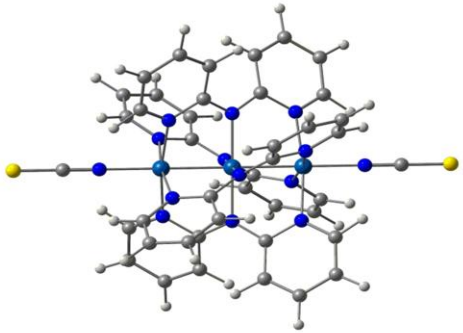


$$H^{(1)} = -\mu_z \varepsilon$$

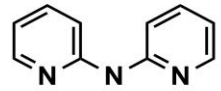
Co_3: finite bias transmission



Chain length: Co_3 vs Co_5?

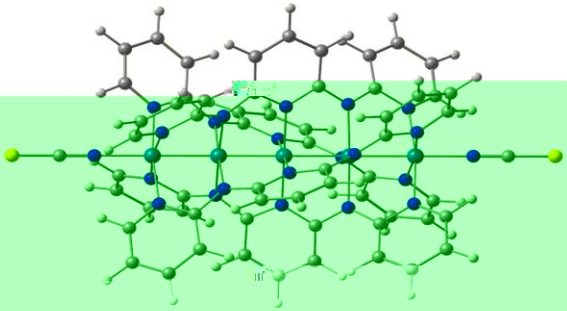


$Co_3(dpa)_4(NCS)_2$

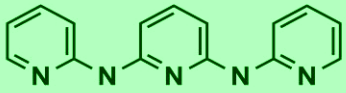


dpa

G* = 530 n*S

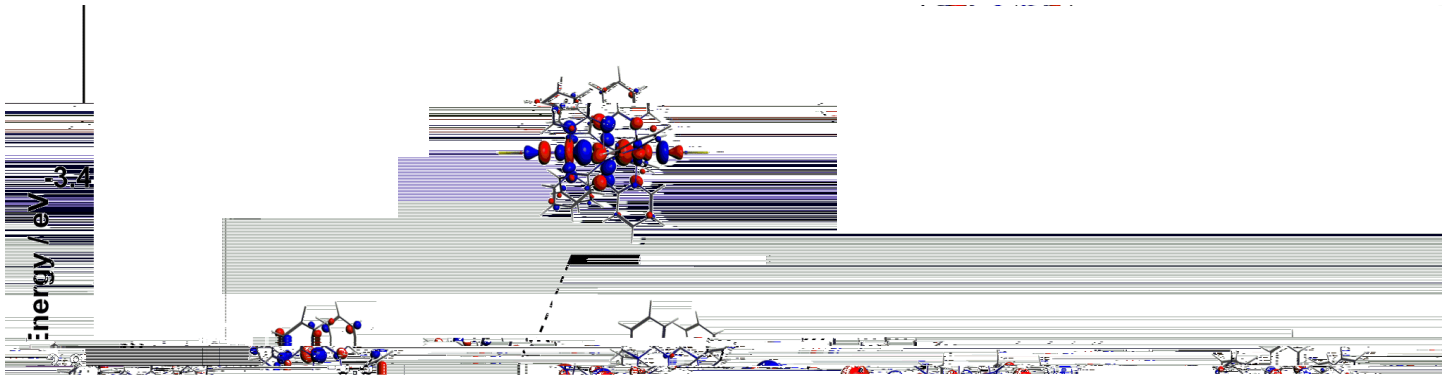


$Co_5(tpda)_4(NCS)_2$



tpda

G* = 100 n*S



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

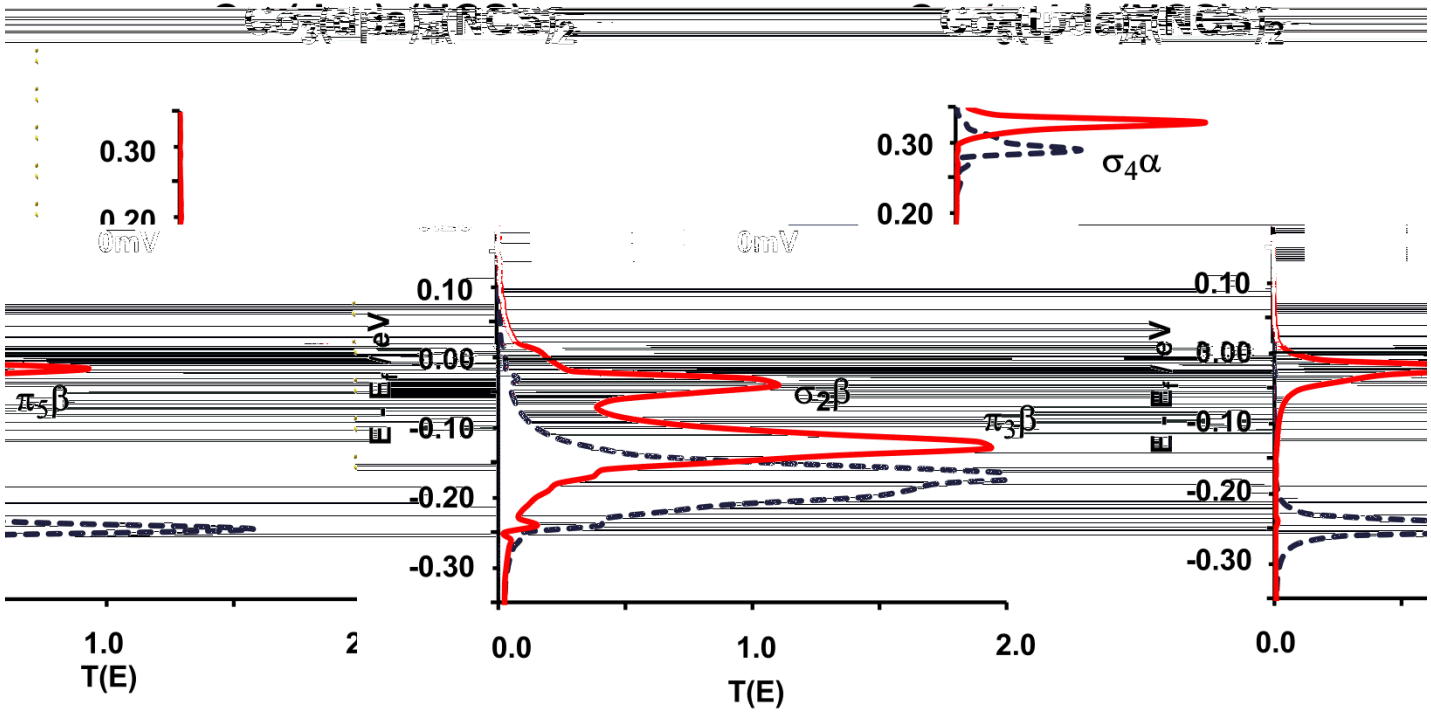
Co-Co = 2.32 Å

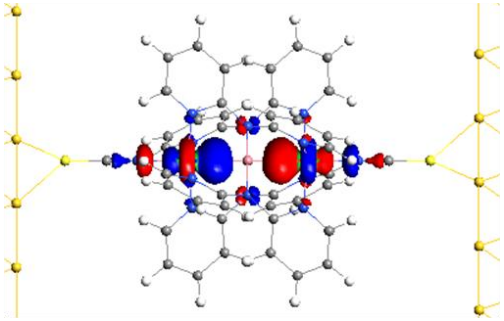
≈ s.o.

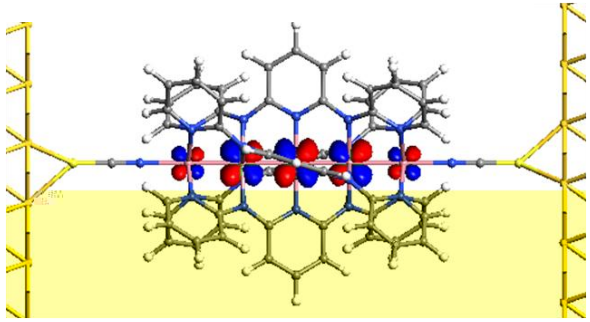
$Co_5(tpda)_4(NCS)_2$
^2E

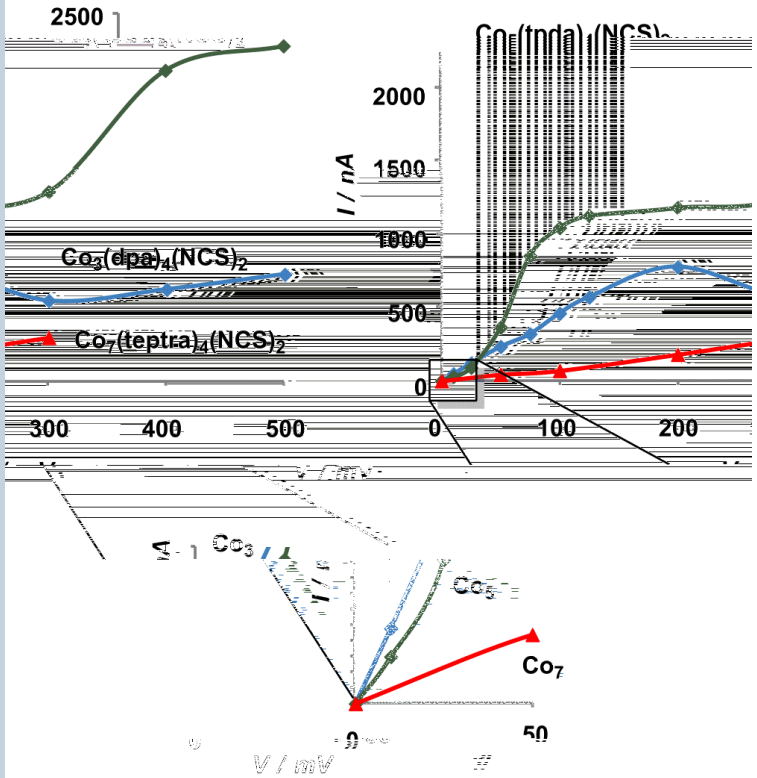
Co-Co = 2.25 Å

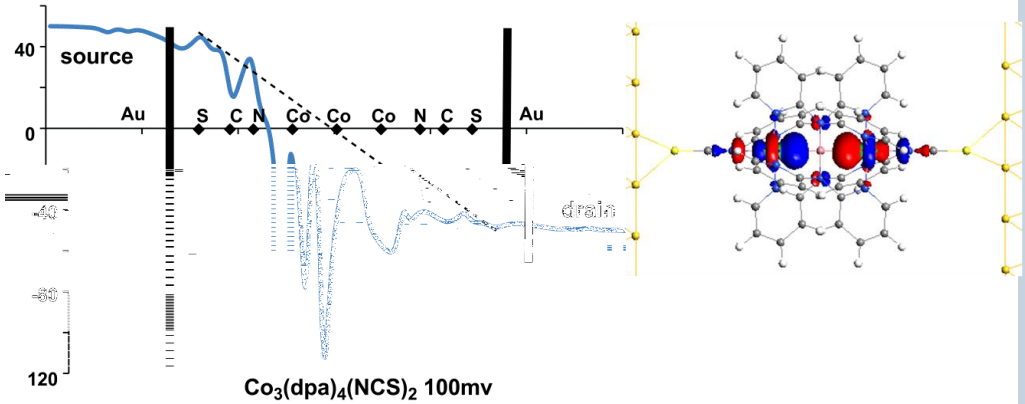
> s.o.

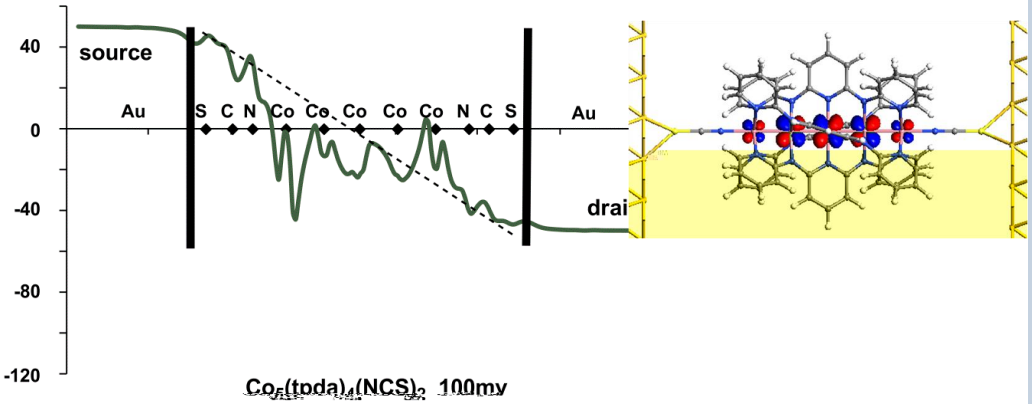

0.30
0.20
$\sigma_4\alpha$
0.10
0.00
-0.10
-0.20
-0.30
eV
E_F
$\pi_5\beta$
$\sigma_2\beta$
$\pi_3\beta$
1.0
T(E)
0.0
1.0
2.0
T(E)
0.0



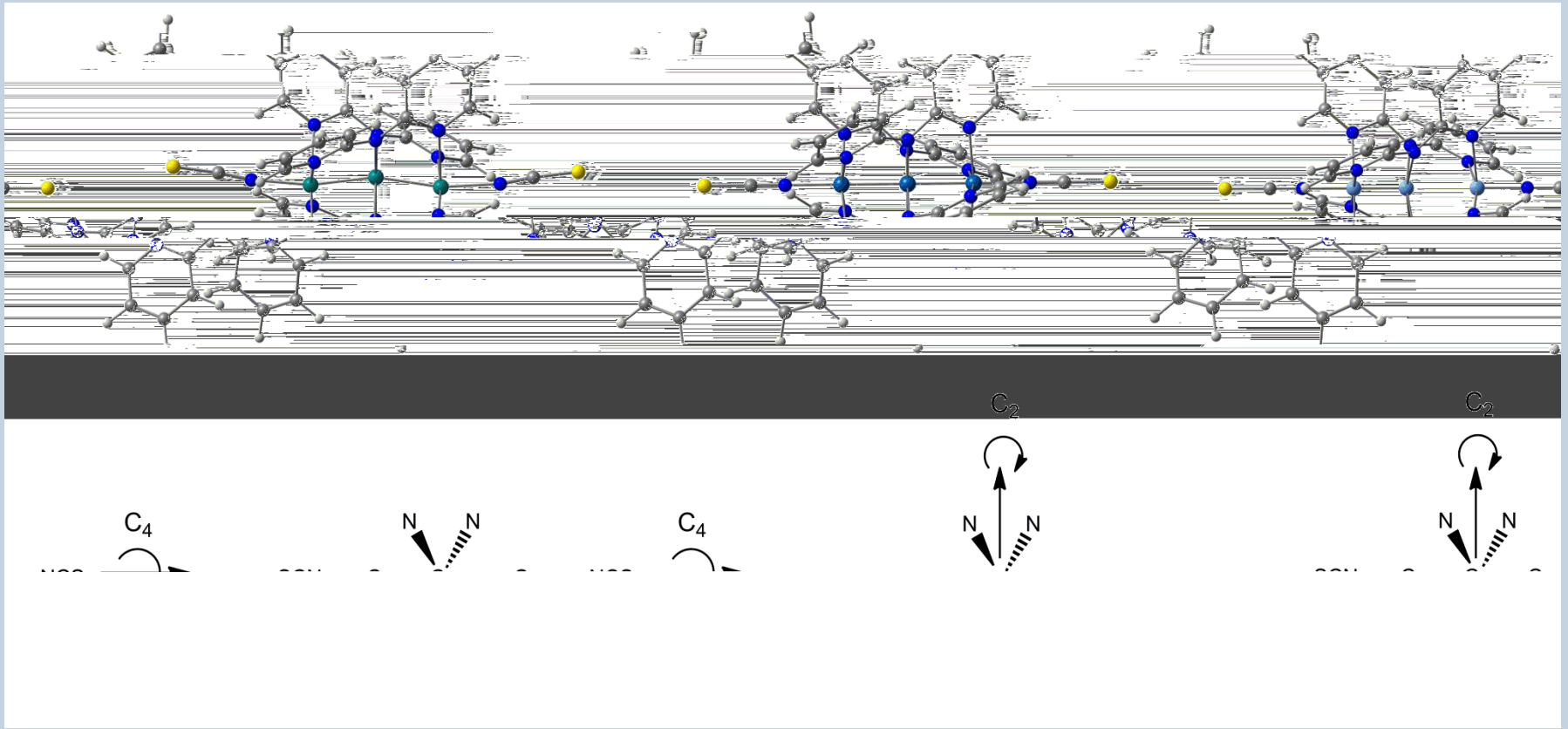



2500
2000
1500
1000
500
0
I / nA
$Co_3(dpa)_4(NCS)_2$
$Co_7(teptra)_4(NCS)_2$
300
400
500
0
100
200
Co_3
Co_5
Co_7
50
V / mV

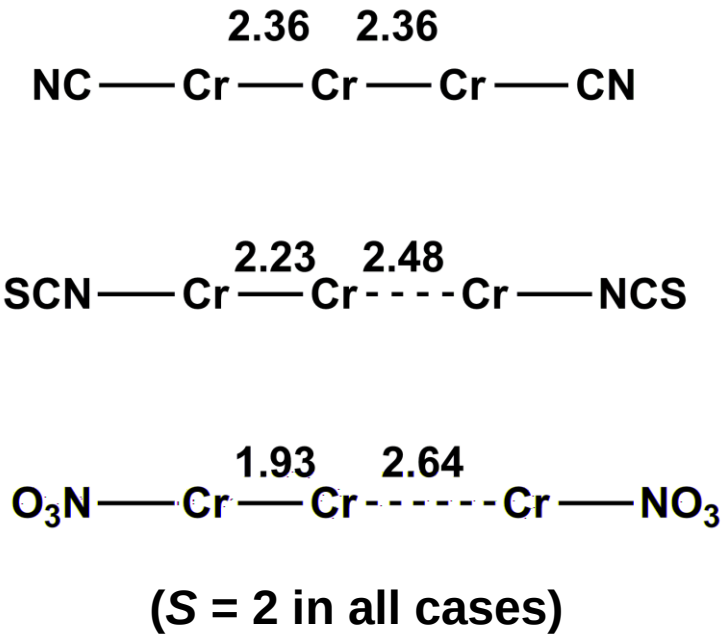

40
0
-40
-80
120
source
Au
S C N Co Co Co N C S
Au
drain
$Co_3(dpa)_4(NCS)_2$ 100mv


40
0
-40
-80
-120
source
Au
S C N Co Co Co Co Co N C S
Au
drai
$Co_5(tpda)_4(NCS)_2$ 100mv

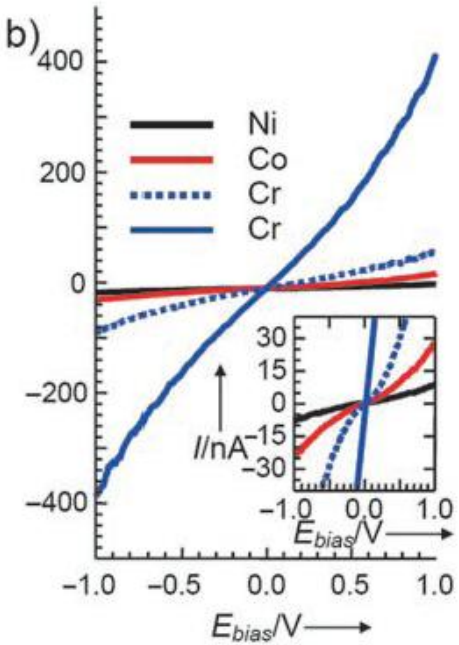
Bends and breaks

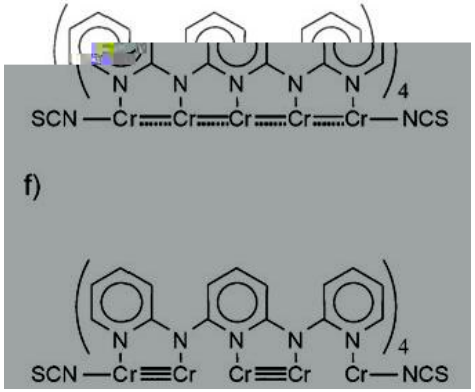


Structural diversity in Cr_3 EMACs



(*S* = 2 in all cases)

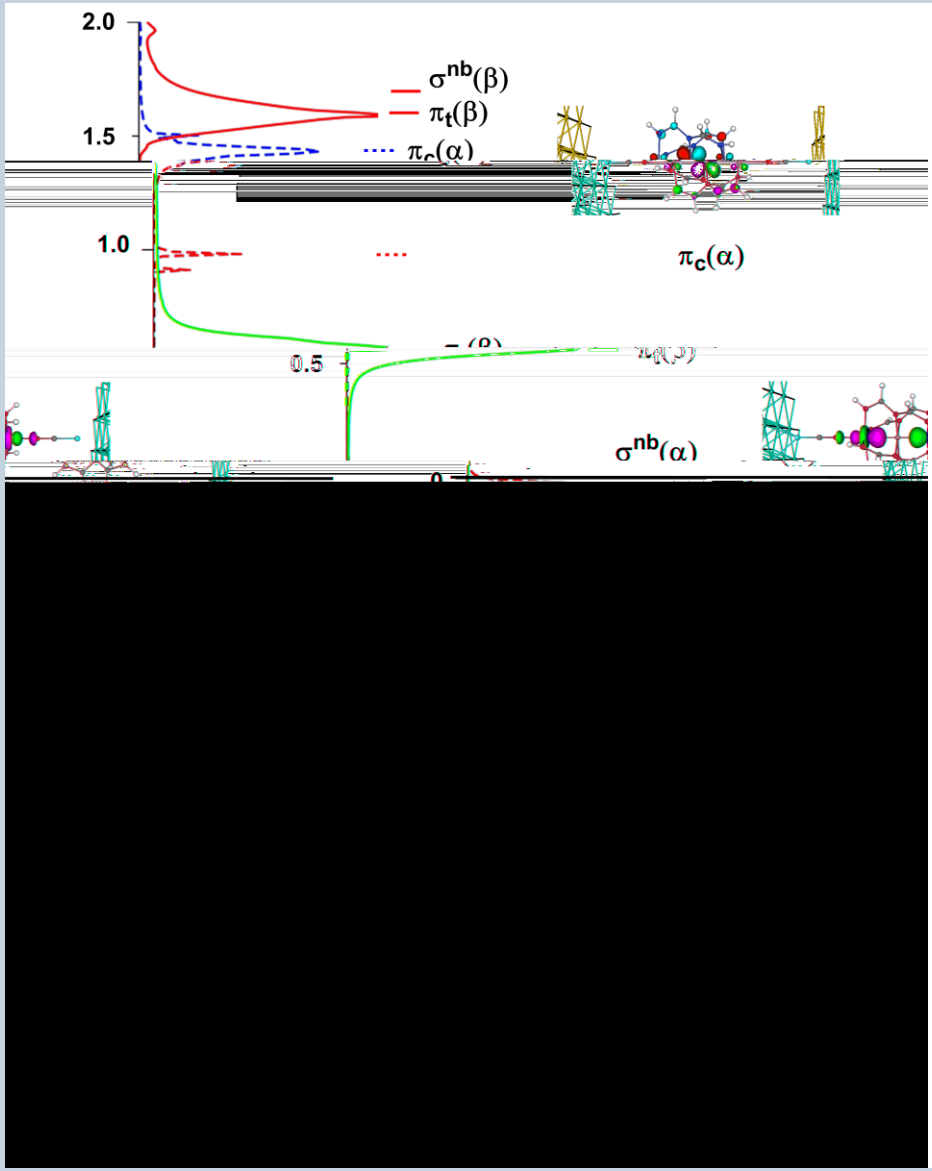


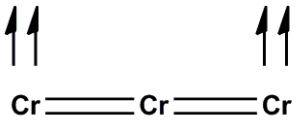


Co_3 vs Cr_3

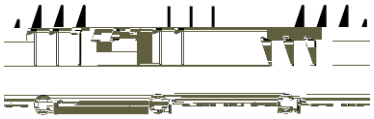
G/ S	STM	c-AFM	DFT
Cr	1.11	0.37	4.48
Co	0.53	0.021	0.42

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

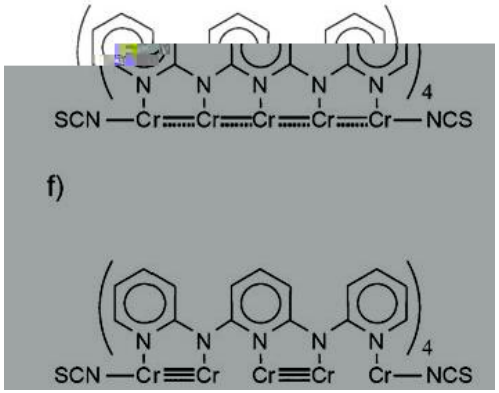


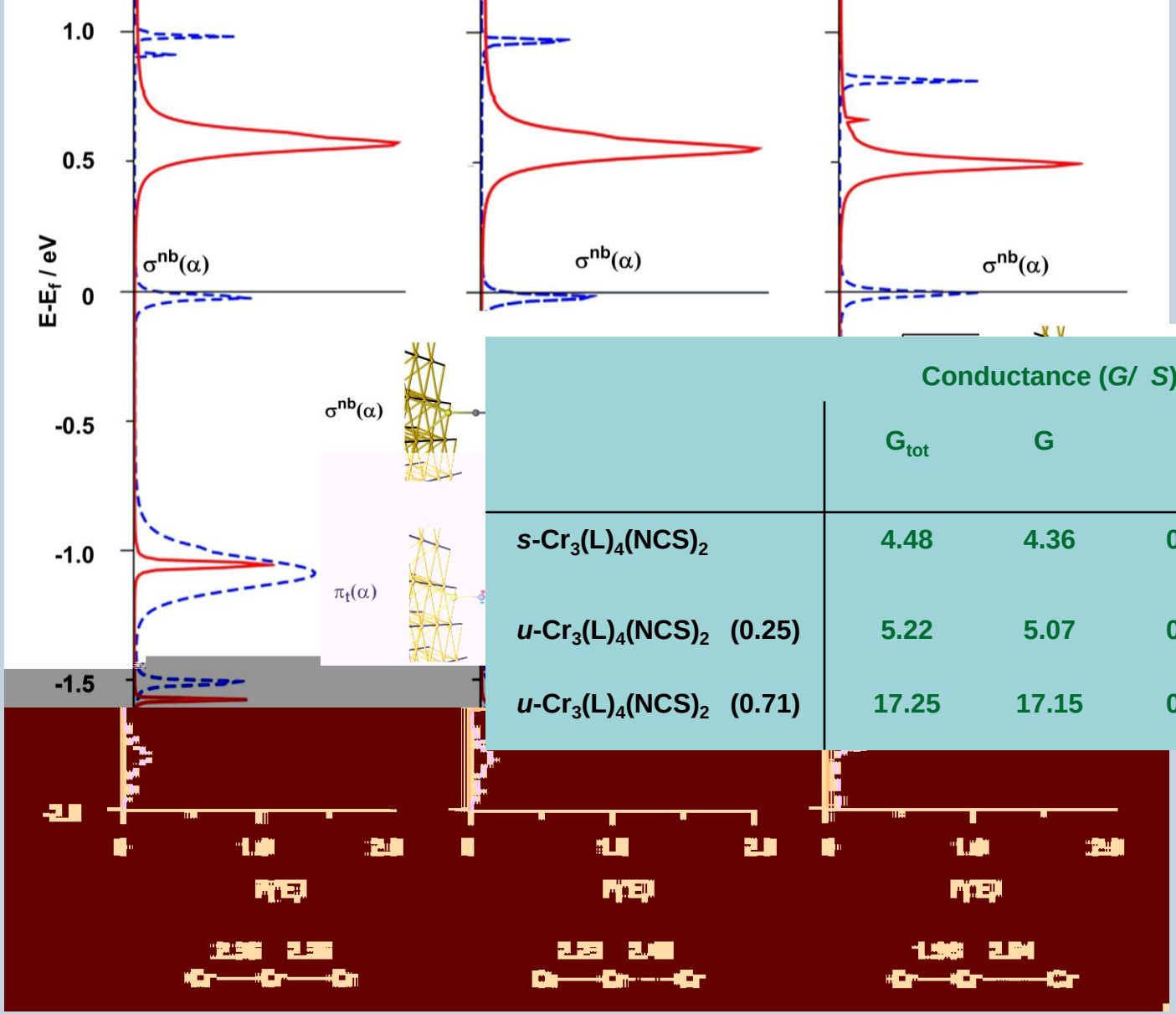


incorrect!



more accurate!





	Conductance (*G*/ *S*)		
	G_{tot}	G	G
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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