

# Order and microstructure in metal-organic coordination polymers

**Norberto Masciocchi**

Dipartimento di Scienza e Alta Tecnologia  
Università dell'Insubria, Como (Italy)  
[norberto.masciocchi@uninsubria.it](mailto:norberto.masciocchi@uninsubria.it)

PDS 2012, Villigen, CH  
November, 27<sup>th</sup> 2012



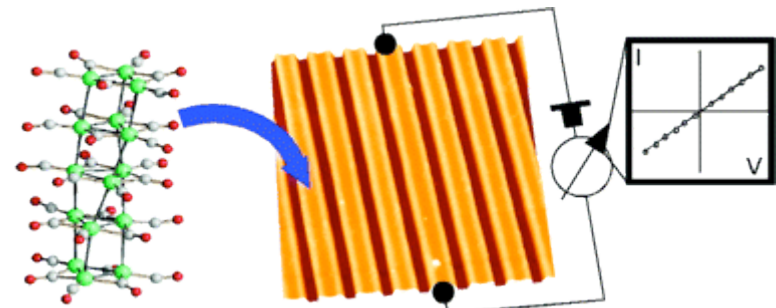
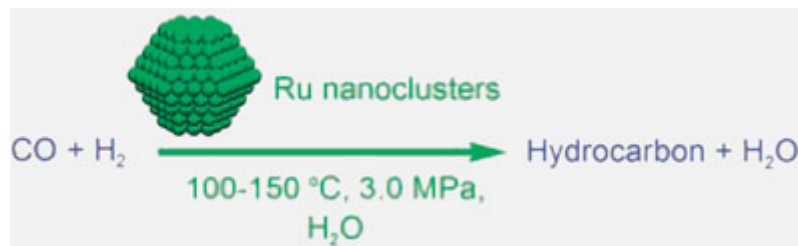
# Outline

- **Structure and Microstructure in Metal Carbonyls**
  - a. **The Information Content in XRPD**
  - b. **The Paracrystalline Model**
- **Structure and Microstructure of MOFs**

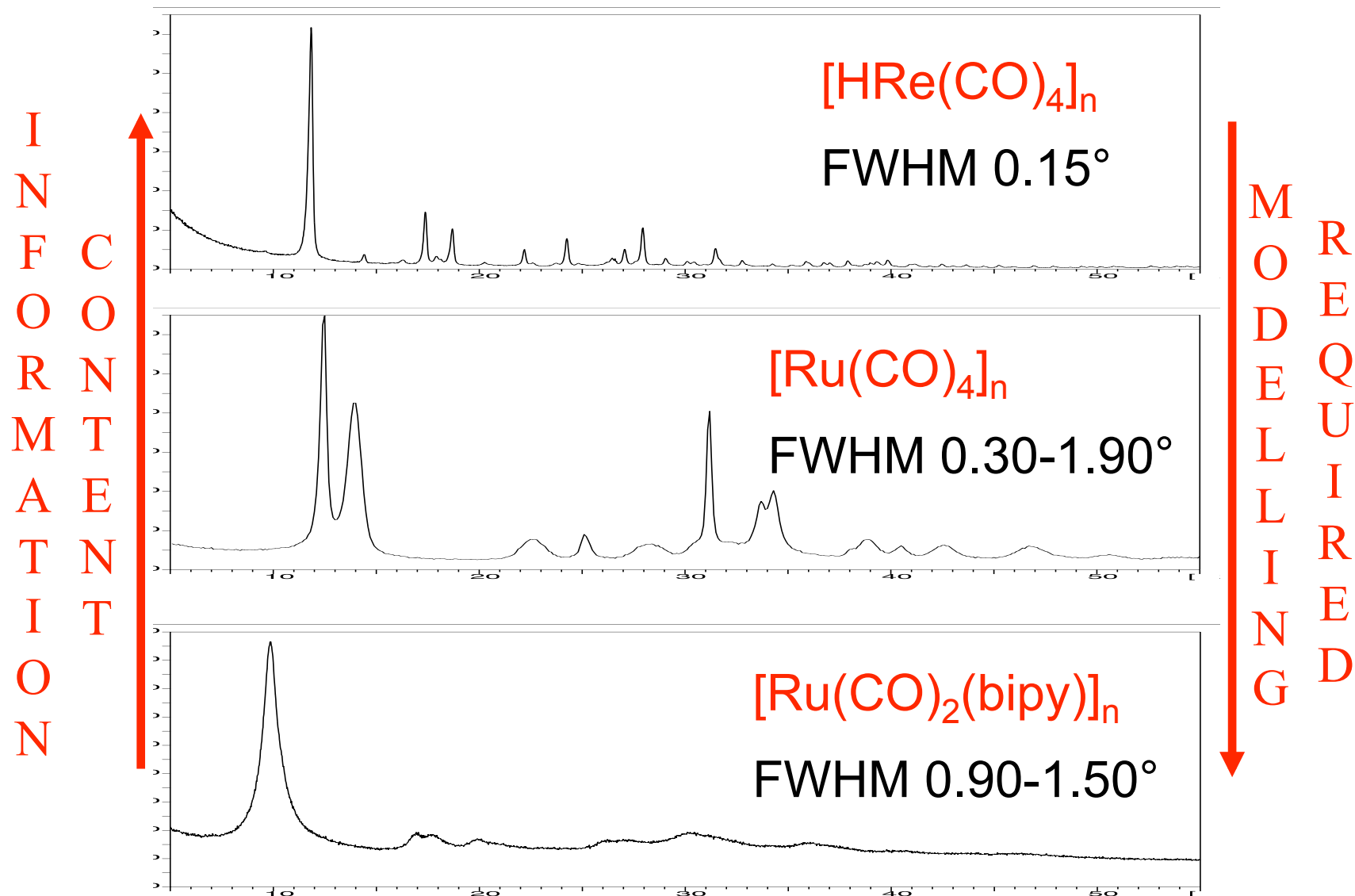
# Metal Carbonyl Clusters

Low valent Metal oxidation states (down to  $-II$ )

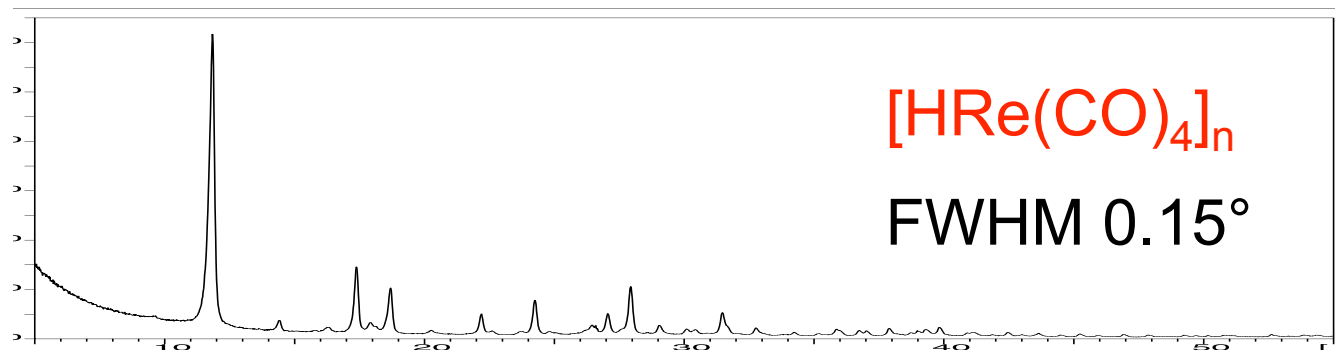
- Ligand unsupported Metal-Metal bonds
- Unprecedented reactivity and structures
- Catalytic, electronic and magnetic properties
- Precursors to NCs, nanowires and CVD thin films



**Structural analysis:** a modelling process where 'external' knowledge is used to improve our comprehension of the regions ill defined by diffraction

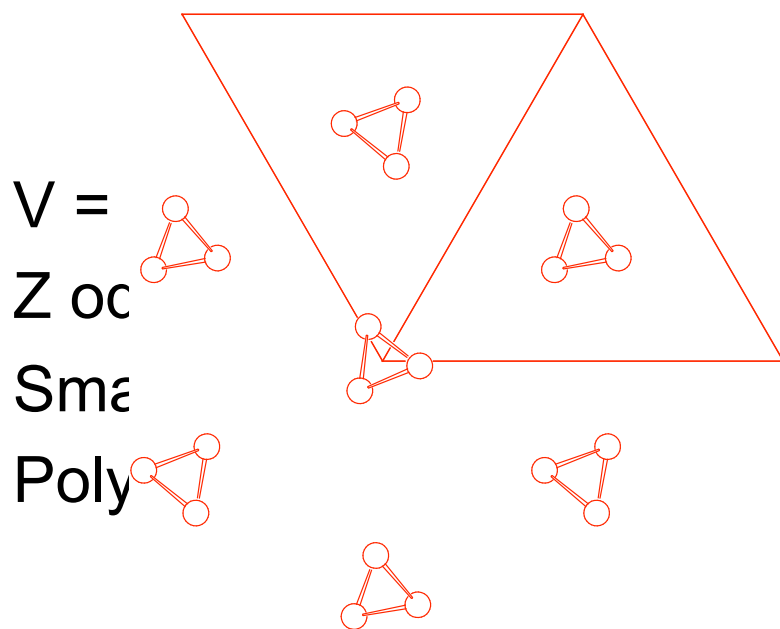
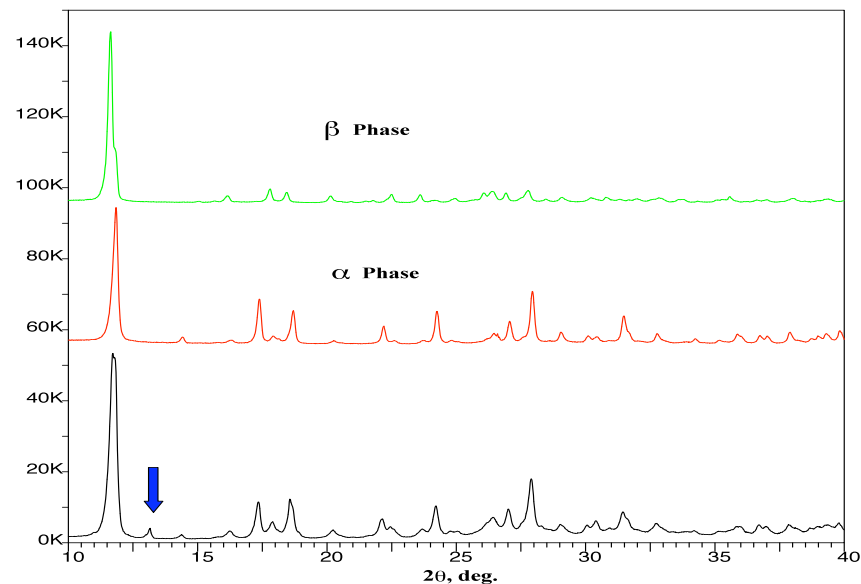
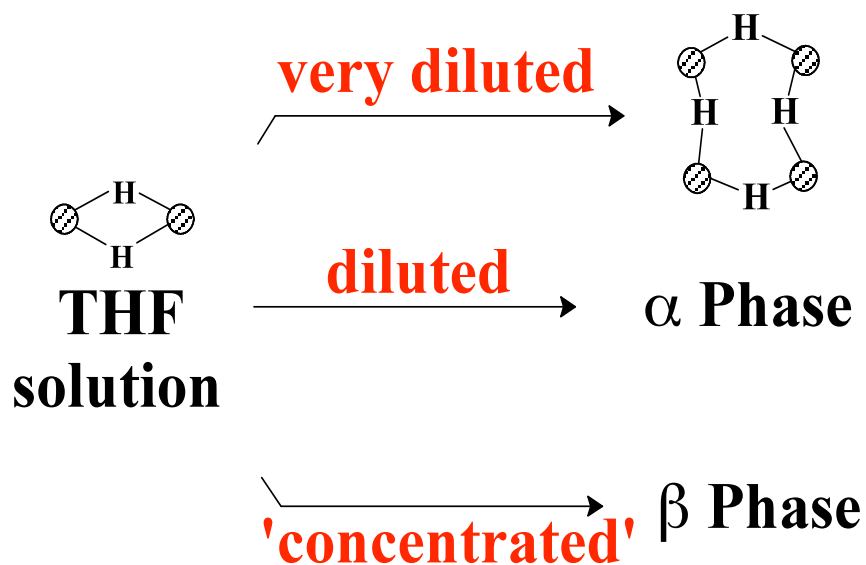


# Good XRPD patterns contain a lot of information



- Indexing, Space Group assignment and Structure Solution are 'relatively easy' tasks.
- Location of light atoms may be problematic
- Refinements require a small number of restraints (linear carbonyls, antibumping conditions)

# Re<sub>2</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub> decomposes in THF affording a solid mixture

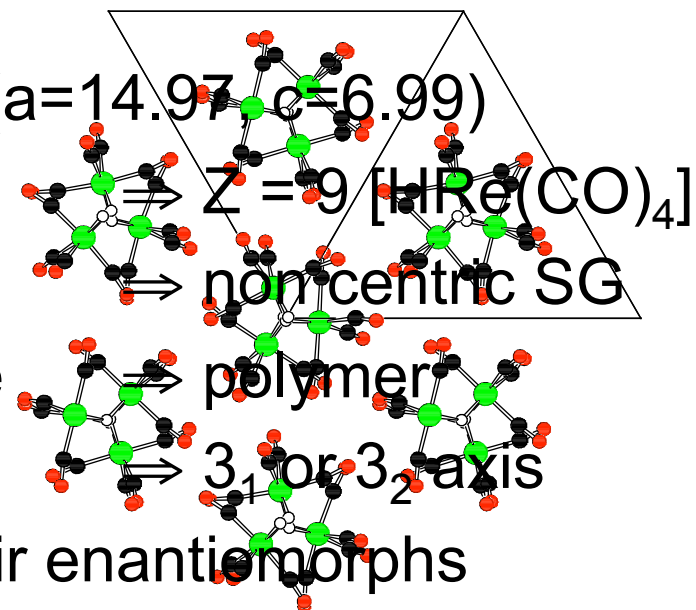


onal cell ( $a=14.97$ ,  $c=6.99$ )

a centre

ar volume

2 and their enantiomorphs



*PD constrained MM minimisation within the crystal lattice*



**PD constraints**

metals from high angles Rietveld refinements

**MM constraints**

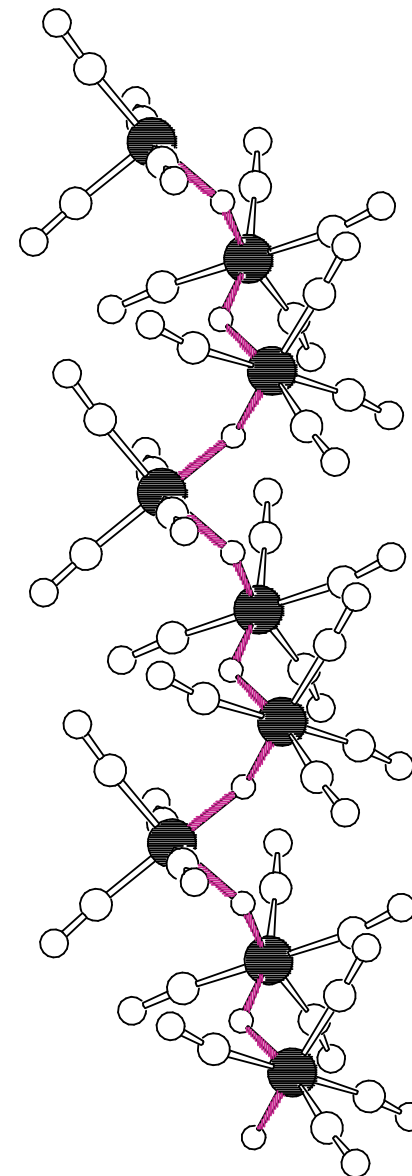
reasonable distances and angles

**Lattice/Space Group constraints**

symmetry related molecules cannot overlap

uniquely determine

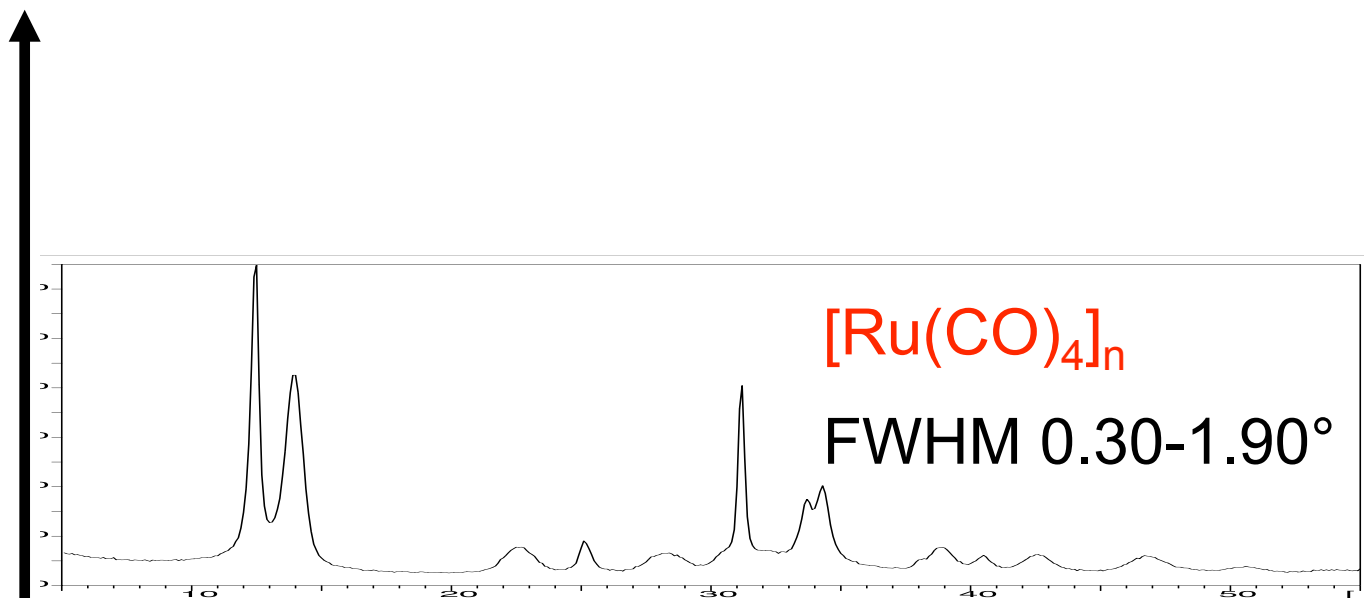
- The shape of the cavity containing the molecule
- The molecular stereochemistry



# Poor XRPD patterns: 'many' broad reflections

Ordered 'crystal structure' in a faulty crystal

INFORMATIONAL

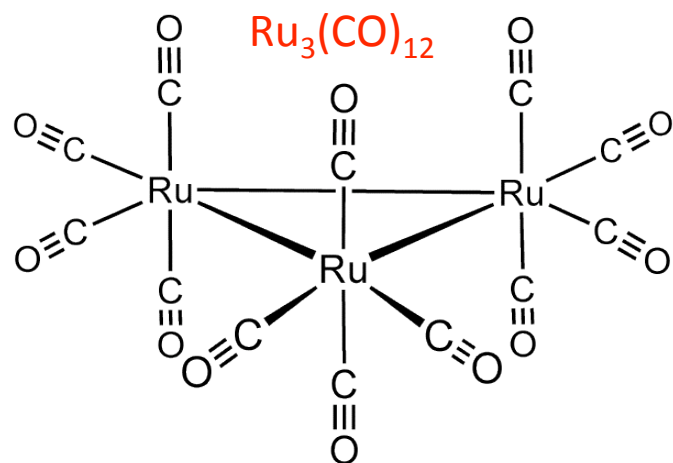


MODELLING REQUIRED

- 'Easy' Indexing
- Space Group assignment **very** ambiguous
- Structure solution problematic
- Light atoms not visible
- Extensive use of rigid fragments



# Ruthenium carbonyls



“There appears to be only one possible example of a polymeric carbonyl, namely  $[\text{Ru}(\text{CO})_4]_n$ ”, F.A.Cotton & G.Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed, 1998, p.1028

## A New Form of Ruthenium Tetracarbonyl

W. Ross Hastings and Michael C. Baird\*

*Inorg. Chem.* **1986**, 25, 2913–2915



Insoluble and Non Volatile Material  
Analytical Data: CHN, Ru, IR, FAB-MS

(XRPD = 5 broad peaks)

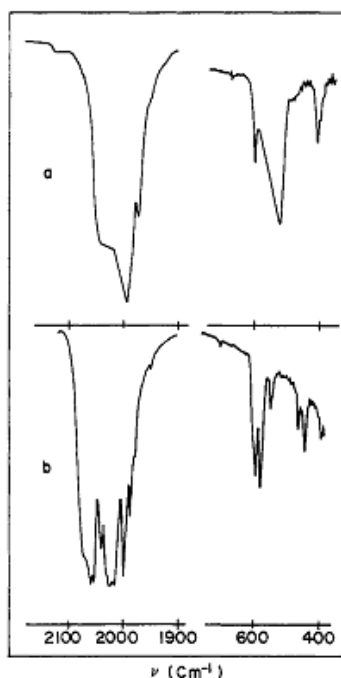
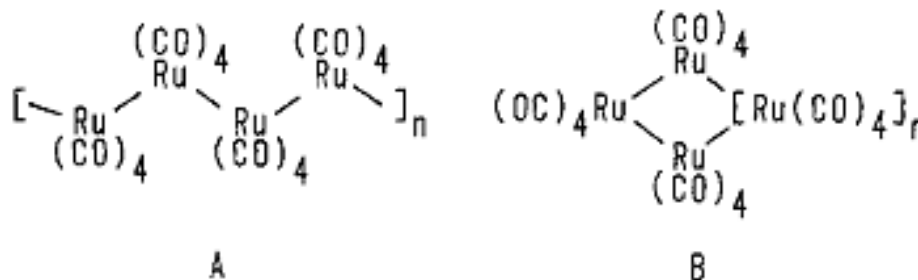


Figure 1. IR spectra (KBr disks) of  $[\text{Ru}(\text{CO})_4]_n$  (a) and  $\text{Ru}_3(\text{CO})_{12}$  (b).

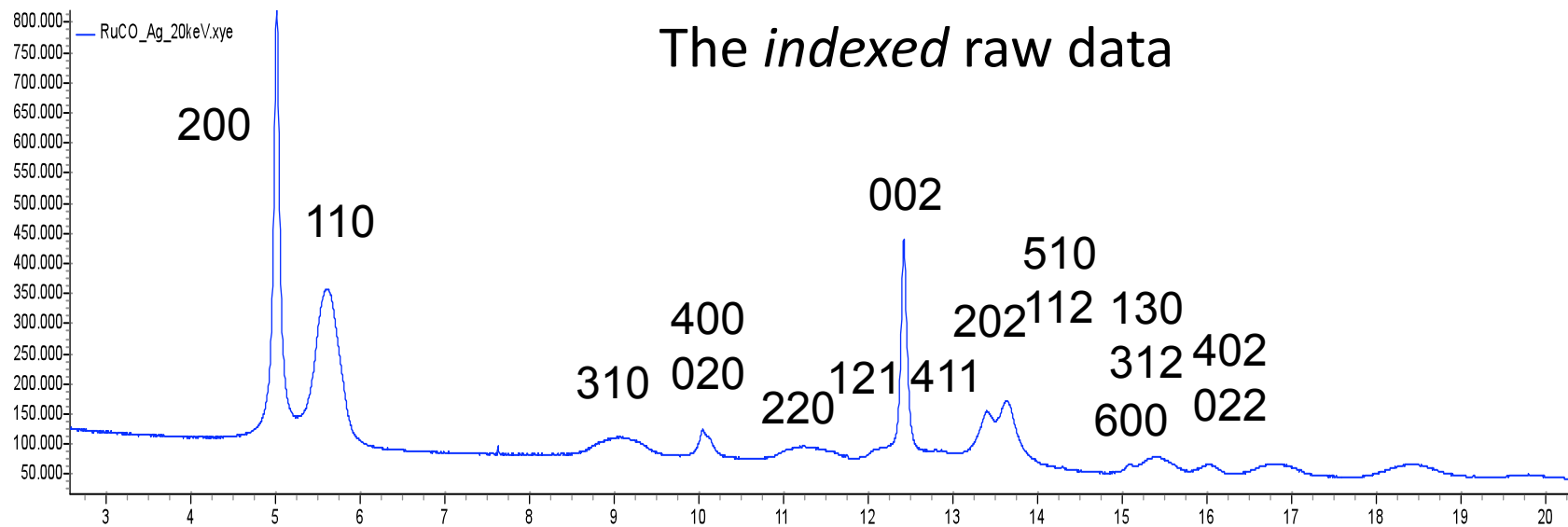


# 8 Years Later...

J. CHEM. SOC. DALTON TRANS. 1993

## Solving Simple Organometallic Structures Solely from X-Ray Powder Diffraction Data: the Case of Polymeric $[\{\text{Ru}(\text{CO})_4\}_n]^{\dagger}$

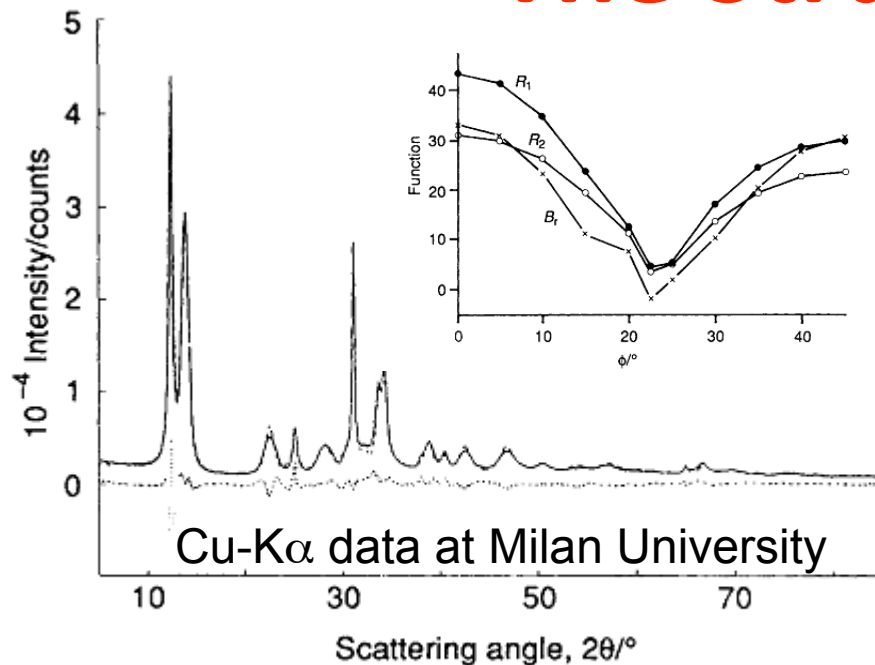
Norberto Masciocchi,<sup>\*,a</sup> Massimo Moret,<sup>a</sup> Paolo Cairati,<sup>a</sup> Fabio Ragaini<sup>b</sup> and Angelo Sironi<sup>\*,a</sup>



Orthorhombic, Space group *Ibam*

$$a = 14.18; b = 7.07; c = 7.54 \text{ \AA}$$

# The Structure

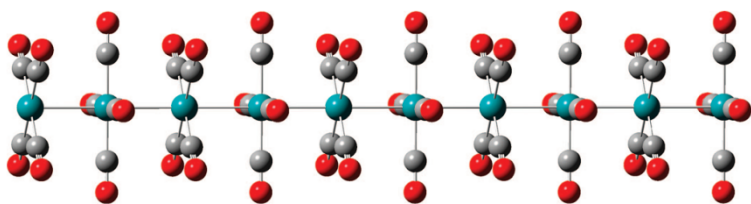


Modified version  
of the DBW 3.2 program

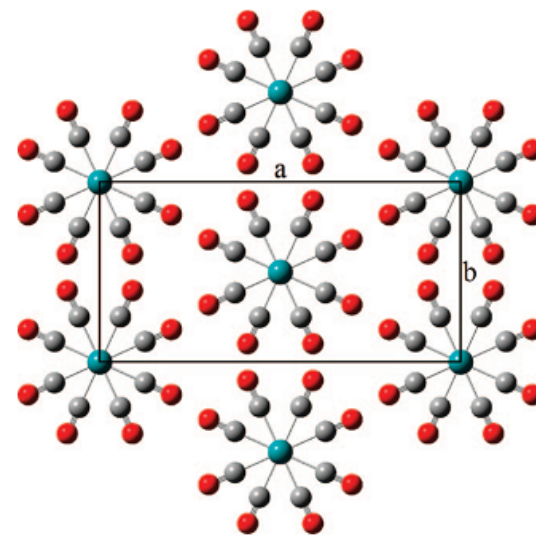


Structure !

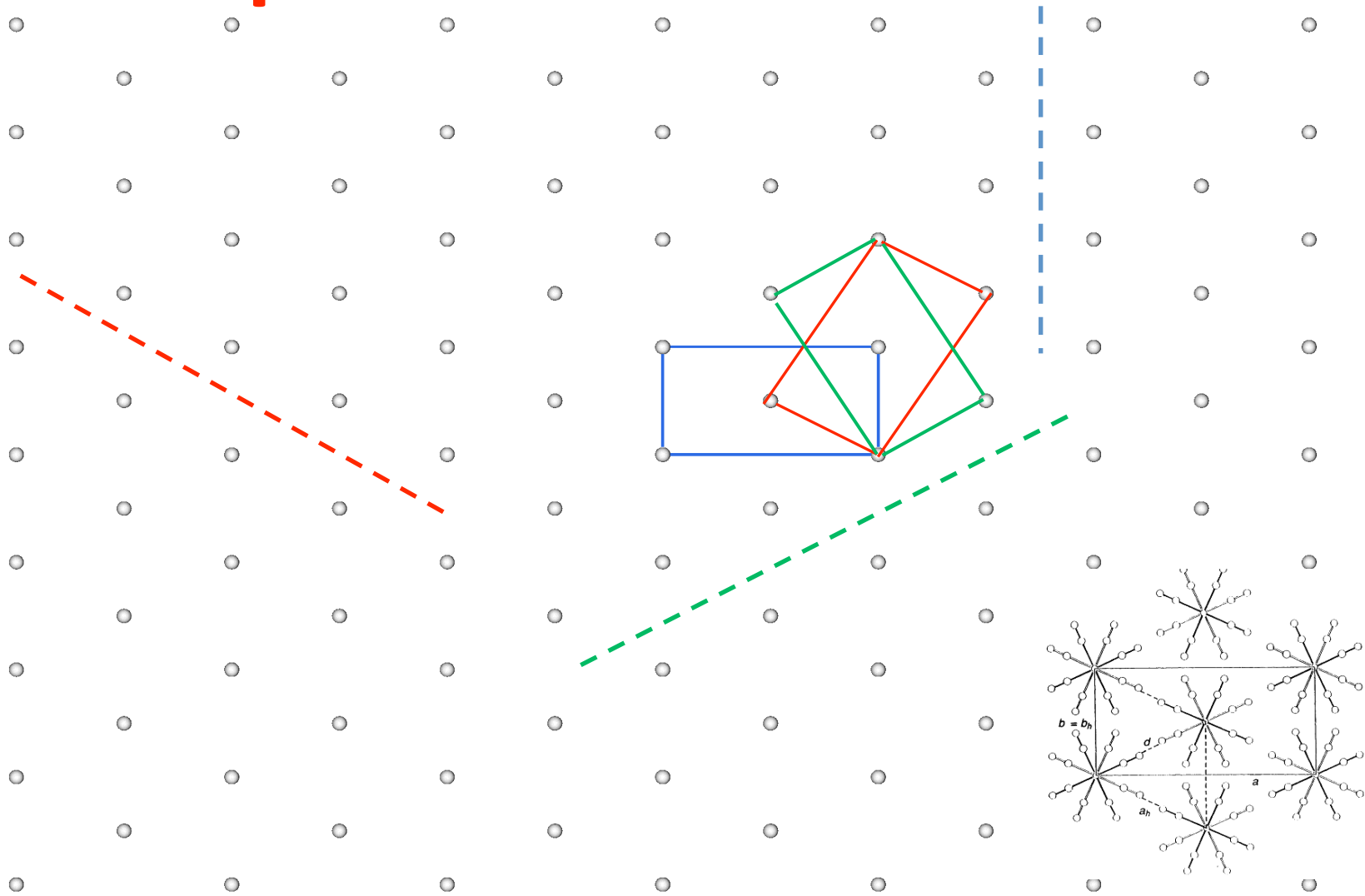
(and phenomenological  
description of anisotropic  
broadening)



Ru-Ru in  $\text{Ru}(\text{CO})_4$  : 2.860(1) Å  
Ru-Ru in  $\text{Ru}_3(\text{CO})_{12}$  : 2.844(2) Å



# Interpretation of the disorder

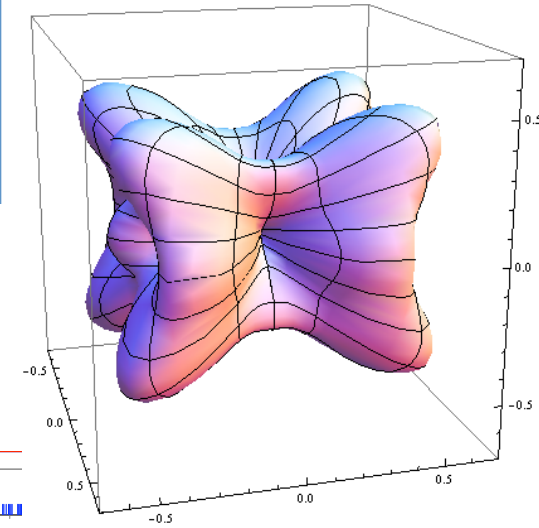
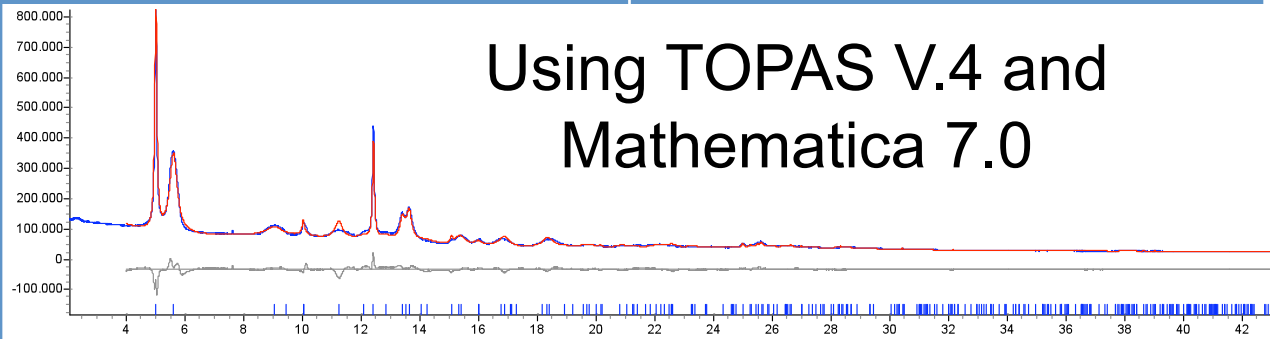


$$L_{hkl}^2 = [h^2 L_h^2 + k^2 L_k^2 + (\tau l)^2 L_l^2] / [h^2 + k^2 + (\tau l)^2]$$

# 20 more Years... new approaches

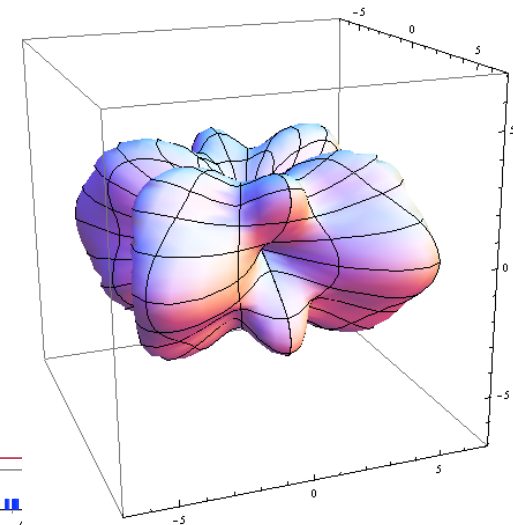
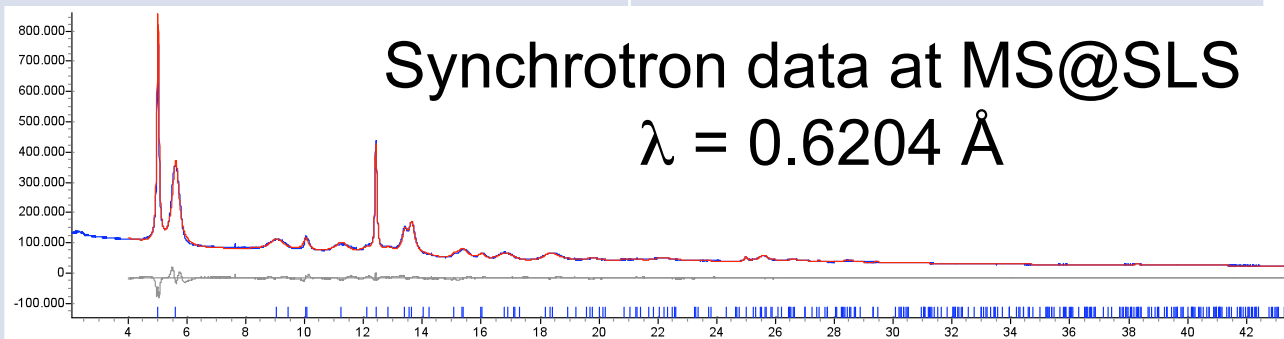
Model 1a,  
8<sup>th</sup> order spherical harmonics  
(size effects:  $1/\cos\theta$ )

$R_{wp} = 0.054$   $R_{Bragg} = 0.039$

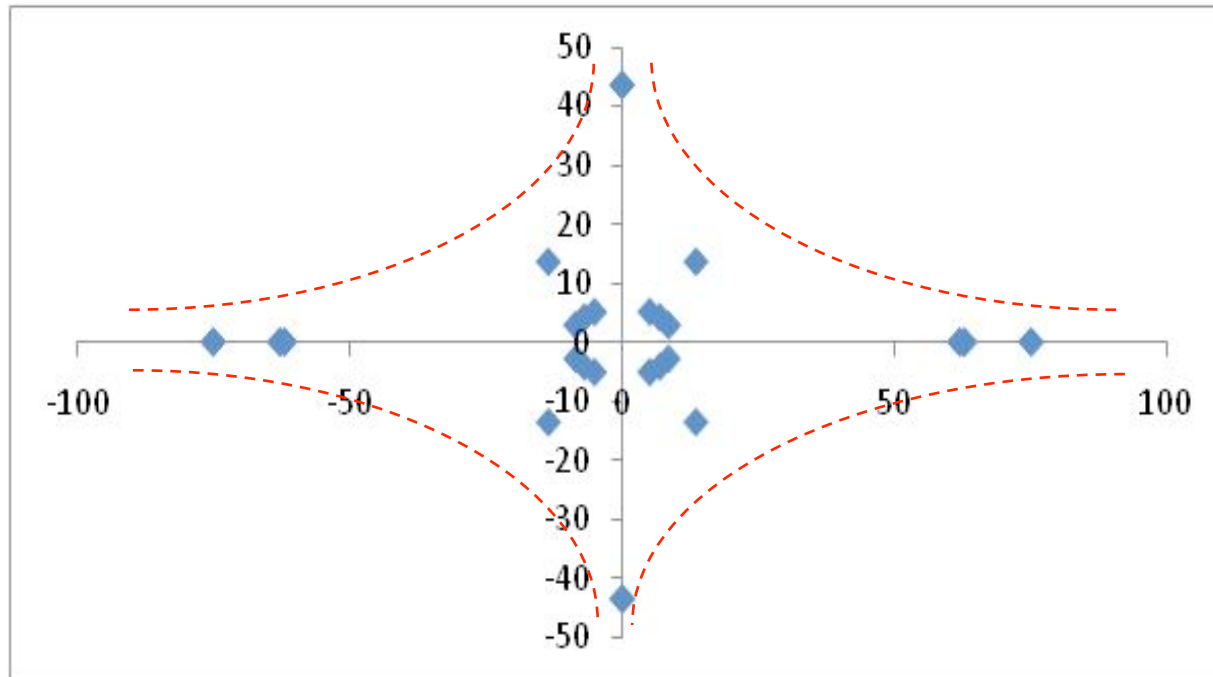


Model 1b,  
8<sup>th</sup> order spherical harmonics  
(strain effects:  $\tan\theta$ )

$R_{wp} = 0.034$   $R_{Bragg} = 0.015$



# Anisotropic spread in peak widths



Plot of the apparent size distribution, derived from unconstrained, individual, profile fitting of the  $hk0$  reflections, drawn in the  $(xy)$  real space

# The Debye Function Approach

The Standard Debye Equation  $I(q) = 2 \sum_{j>i=1}^N b_j b_i \frac{\sin(2\pi q d_{ij})}{2\pi q d_{ij}}$

The Paracrystalline Correction (for correlated motions)  
in the Debye Equation

$$I(q) = 2 \sum_{j>i=1}^N b_j b_i \frac{\sin(2\pi q d_{ij})}{2\pi q d_{ij}} e^{-\frac{1}{2}(2\pi q s_{ij})^2}$$

Paracrystalline correction

This correction has been implemented in the **DEBUSSY Suite**

## Sequence of steps:

- the average periodic structural model is supplied
- an analytical **disordering law** is defined (see following)
- a tailored computational procedure, affecting the sampled distances histogram, has been coded

# 2D displacements of a 2D lattice

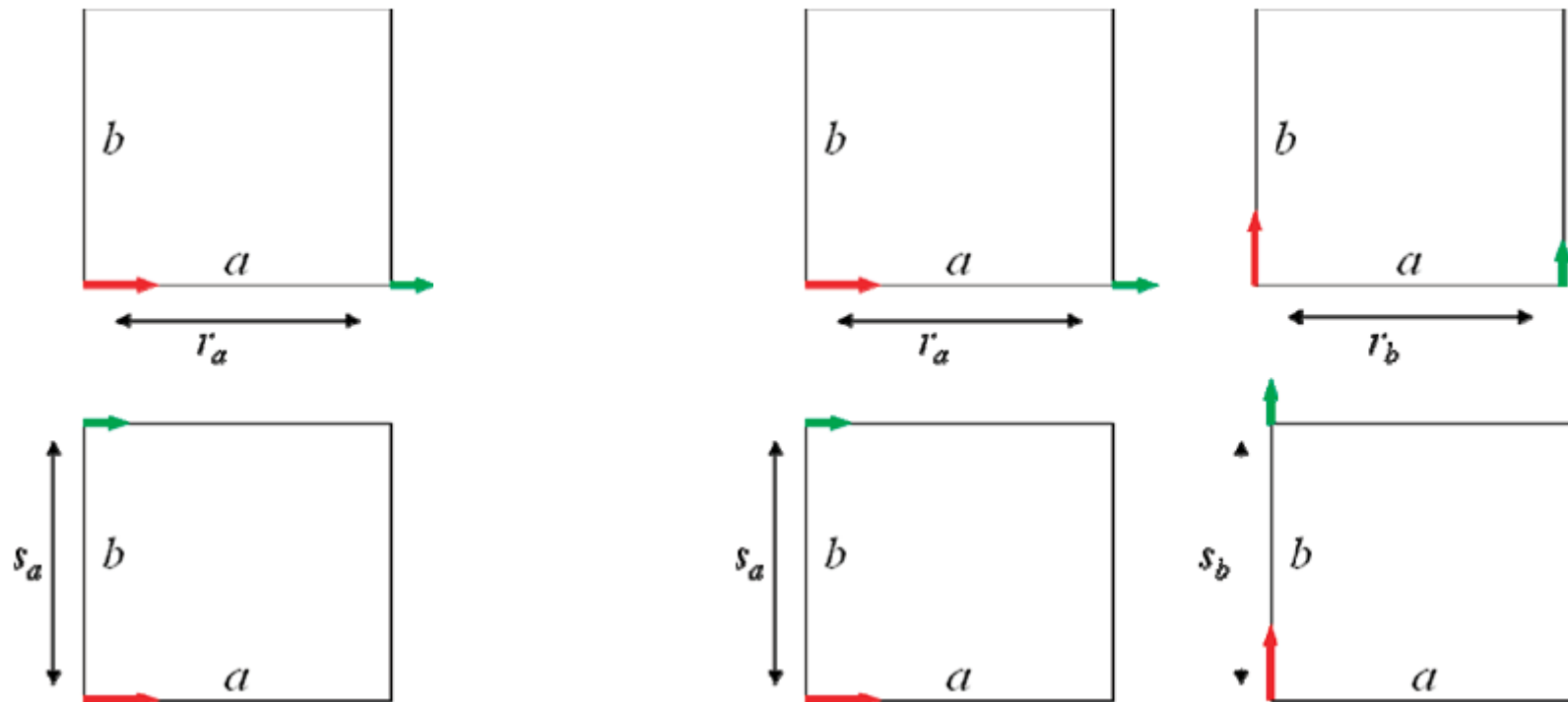
$r_a$  = longitudinal correlation coefficient along  $x$

$s_a$  = transversal correlation coefficient along  $x$

$s_b$  = longitudinal correlation coefficient along  $y$

$r_b$  = transversal correlation coefficient along  $y$

$C_{xy}$  = cross-correlation coefficient



$$P_a(\mathbf{d}) = K_a \times \exp\left(-\frac{1}{2} \frac{(\mathbf{d} - \mathbf{d}_0)^2}{2\sigma_a^2(1 - r_a^{|\mathbf{d}|} s_a^{|\mathbf{d}|})}\right)$$

$$P(\mathbf{d}) = K \exp\left(-\frac{1}{2} \mathbf{v} \cdot \mathbf{C}^{-1} \mathbf{v}\right) \quad \mathbf{v} = \mathbf{d} - \mathbf{d}_0$$

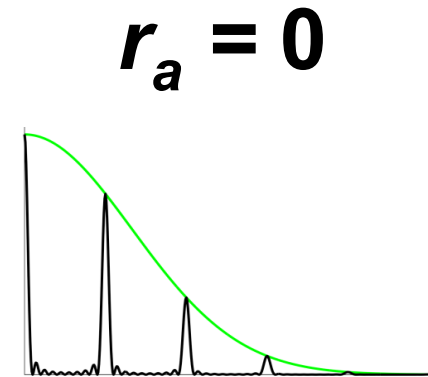
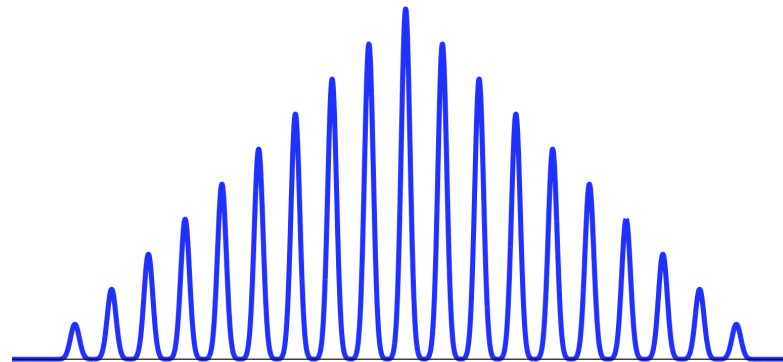
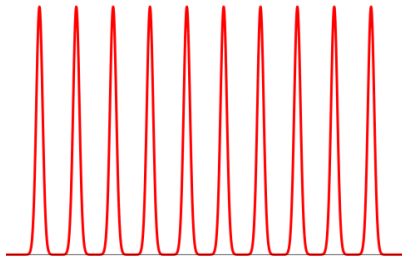


# Scattering in 1D: Correlated motions

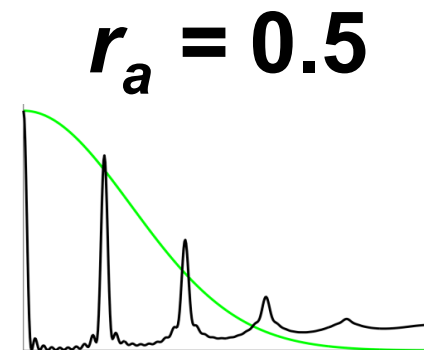
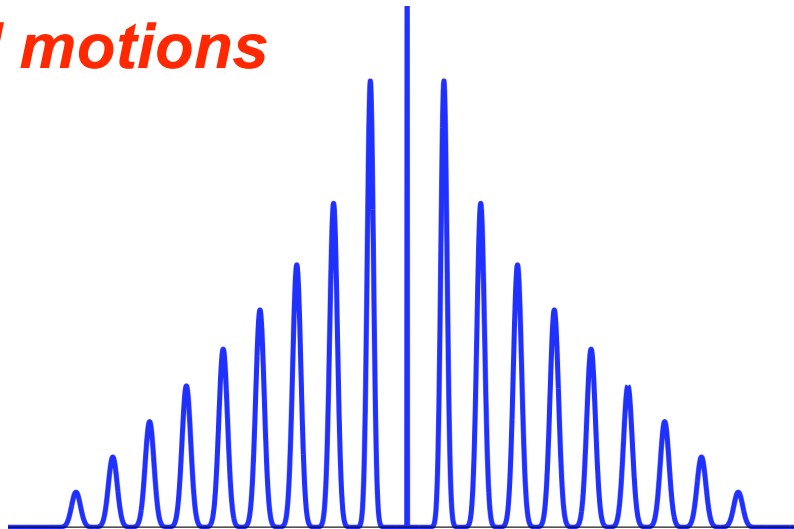
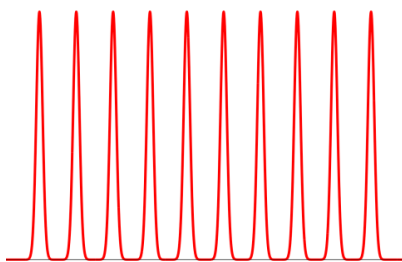
Electron Density

Patterson Function

Scattered Intensity



***Uncorrelated motions***



**Correlated motions**

# Scattering in 2D: Correlated motions

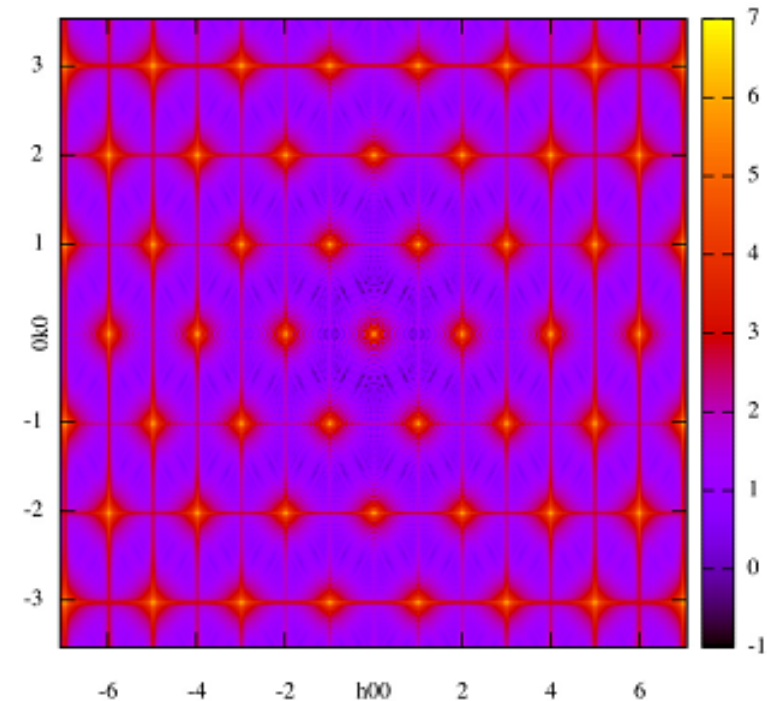
## 2-D net, 2-D displacements

$\sigma_a$  and  $\sigma_b$  amplitudes

**Five**  $r_a, s_a, r_b, s_b, c_{xy}$  parameters in matrix  $\mathbf{C}$

$$\mathbf{C} = \begin{pmatrix} \hat{\sigma}_a^2 & \hat{\sigma}_a \hat{\sigma}_b c_{xy} \\ \hat{\sigma}_a \hat{\sigma}_b c_{xy} & \hat{\sigma}_b^2 \end{pmatrix}$$

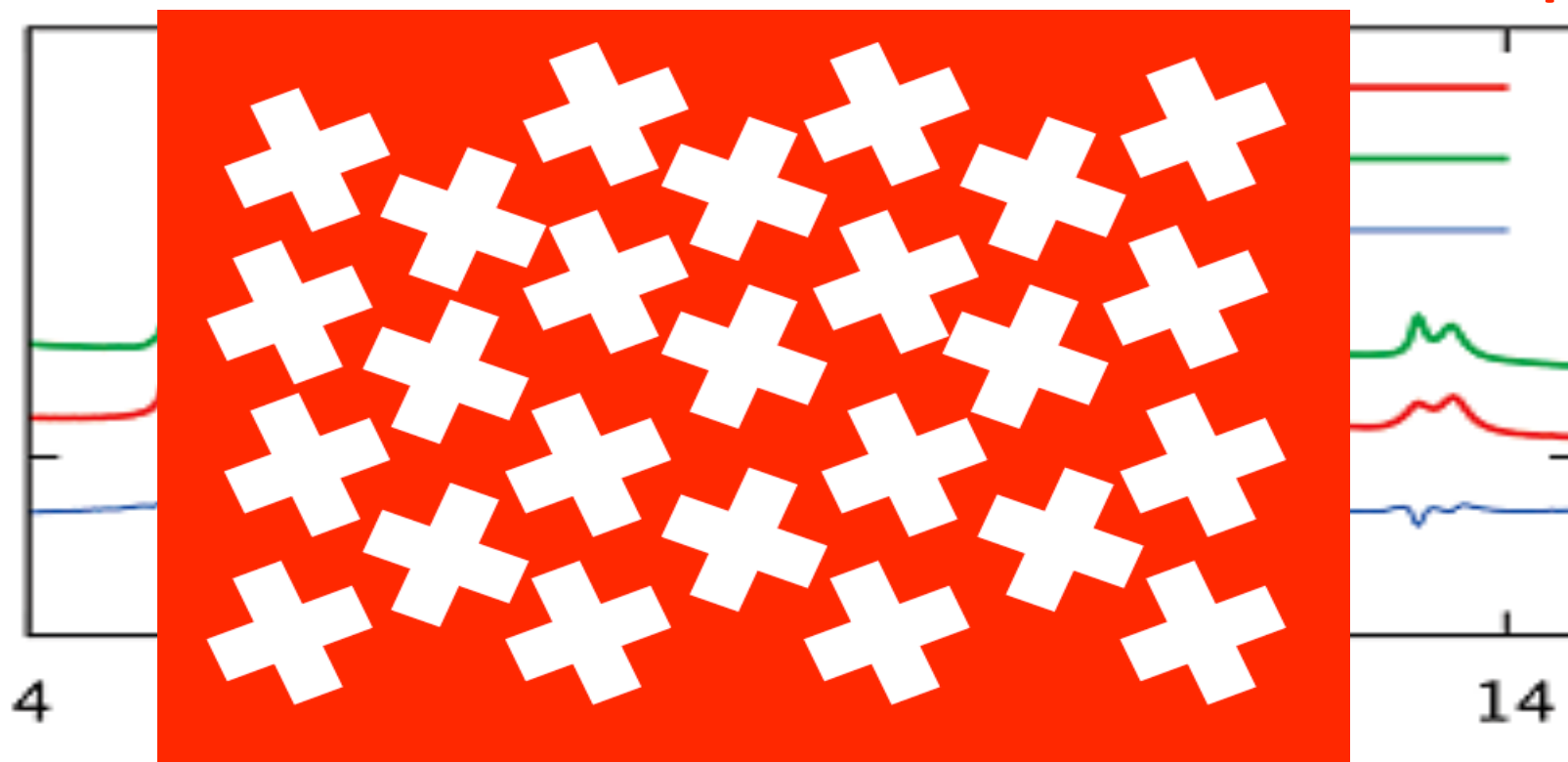
$$P(\mathbf{d}) = K \exp\left(-\frac{1}{2} \mathbf{v} \cdot \mathbf{C}^{-1} \mathbf{v}\right) \quad \mathbf{v} = \mathbf{d} - \mathbf{d}_o$$



$$r_a = 1.00, \quad r_b = 0.97, \quad s_a = 0.97, \quad s_b = 1.00, \quad c_{xy} = 0, \quad \sigma_x = \sigma_y = 3.0 \text{ \AA}$$

**From actual  $[\text{Ru}(\text{CO})_4]_n$  refinement**

# The Paracrystalline Model for $[\text{Ru}(\text{CO})_4]_n$



## Derived DF microstructural parameters:

Average size in **a,b** = 50 nm

Average size along **c** = 44.7(15.4) nm

$\sigma_a = \sigma_b$  = 0.3 nm



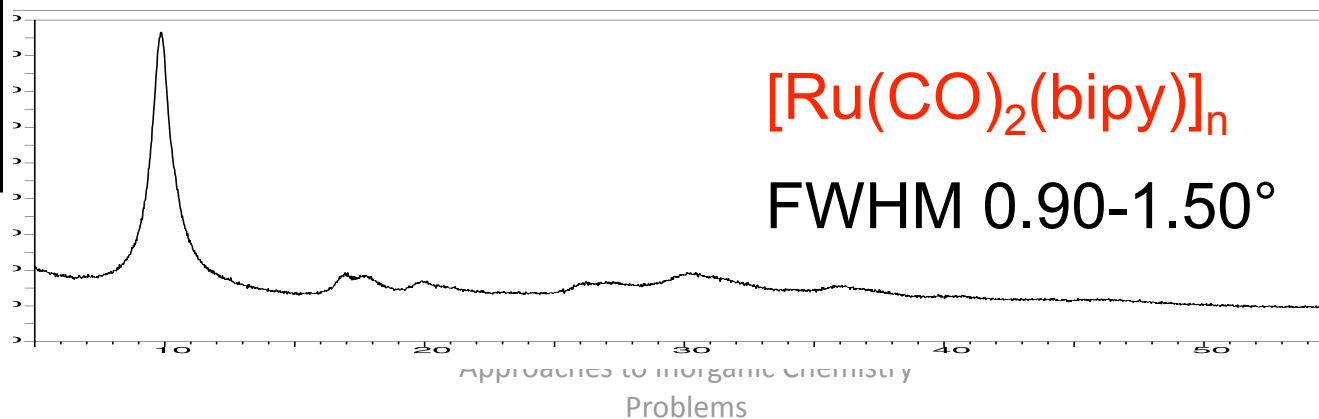
# Poor XRPD patterns: a few, if any, broad reflections

Disordered 'crystal structure' in a faulty crystal

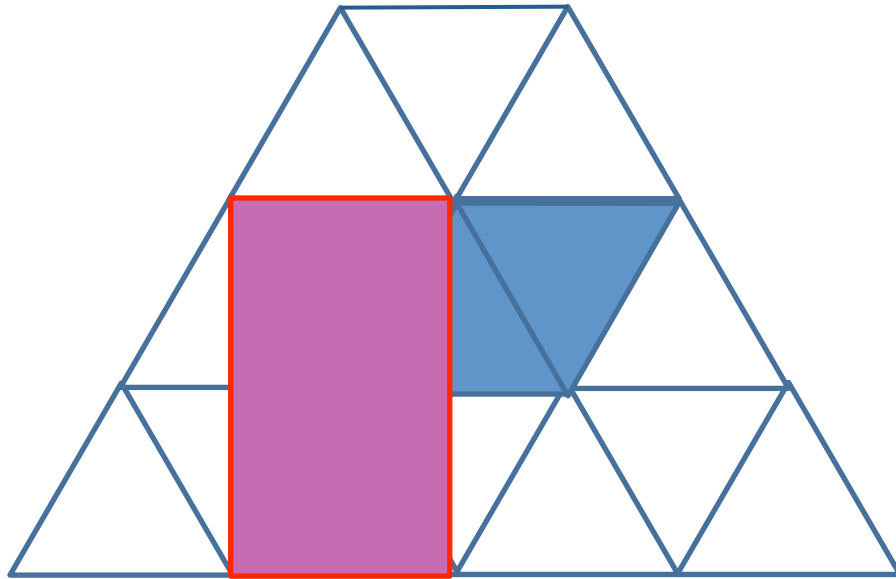
INFORMATIONAL

- Indexing, Space group assignment and Structure Solution are ambiguous
- Analogies with known 'related' phases helps

MODELLING REQUIRED



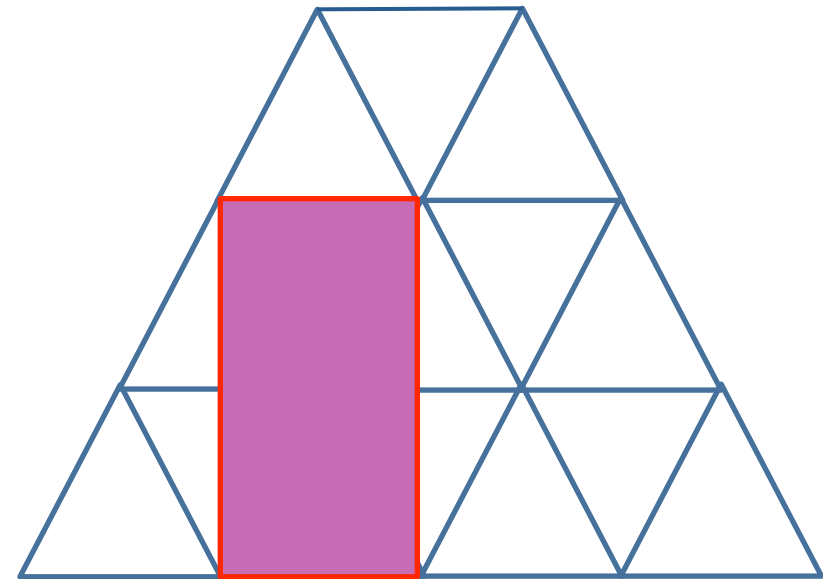
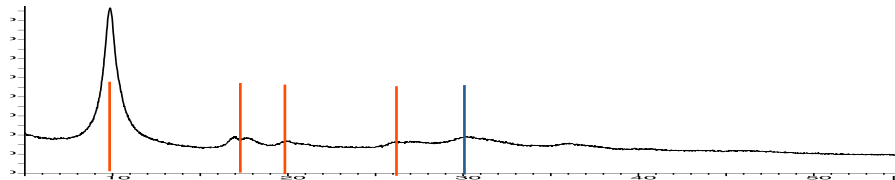




In the ab plane,  $a = b = 10.2 \text{ \AA}$ ,  $\gamma = 120^\circ$

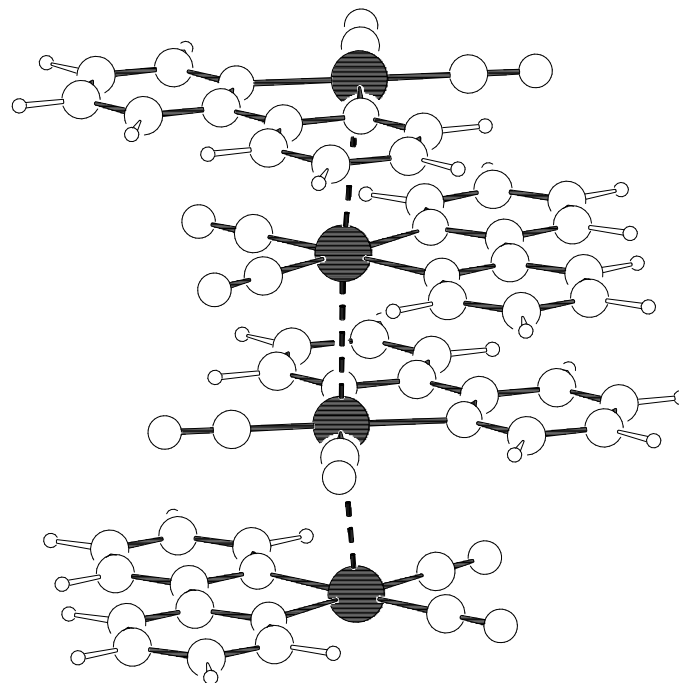
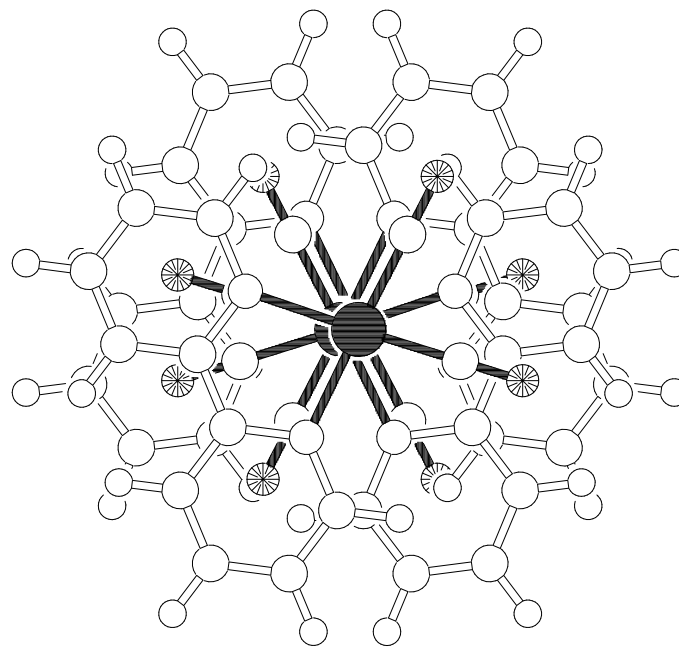
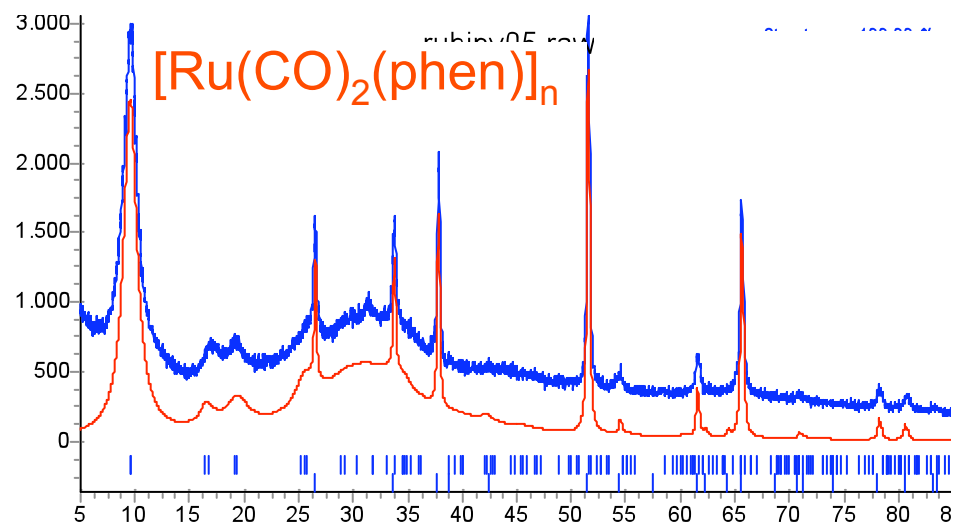
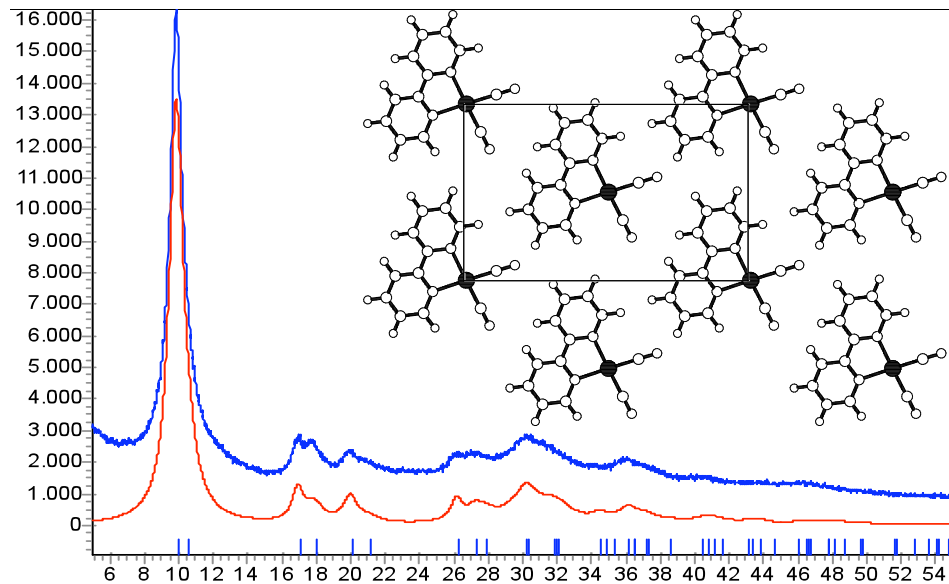
An alternative description exists, with  
 $a = 10.2 \text{ \AA}$ ,  $b = \sqrt{3}a = 17.66 \text{ \AA}$ ,  $\gamma = 90^\circ$   
 (C-centered)

Splitting of the peaks requires  
 $a = 10.4 \text{ \AA}$ ,  $b = 16.8 \text{ \AA}$ ,  $\gamma = 90^\circ$  (C-centered)

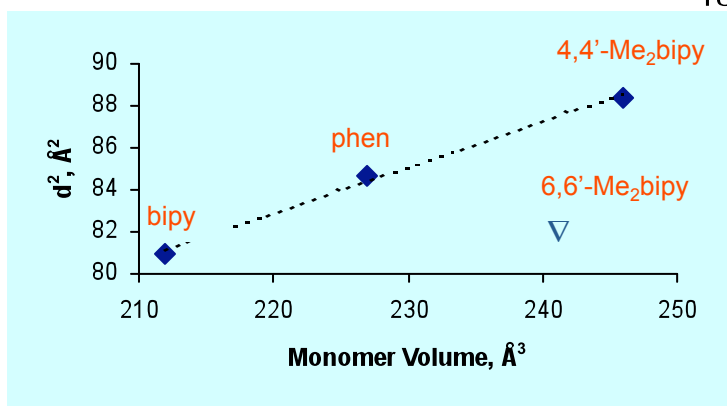
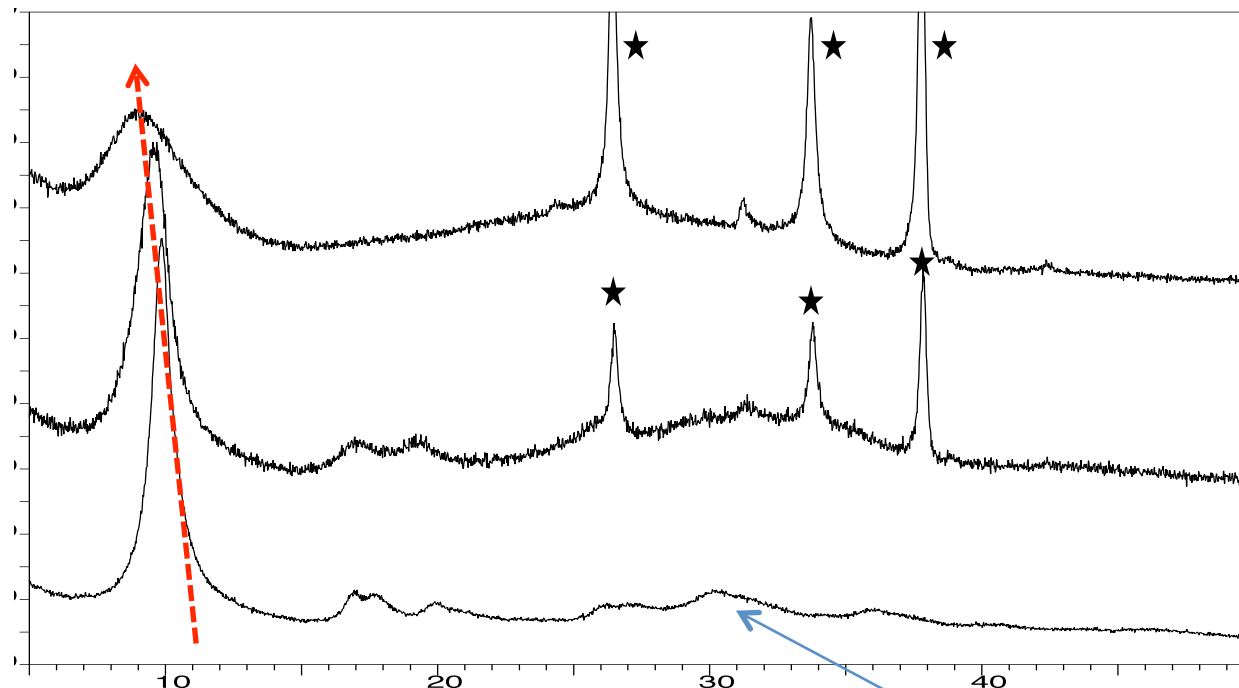
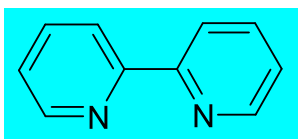
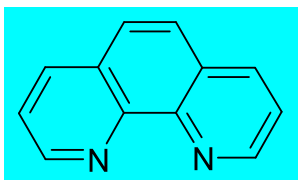
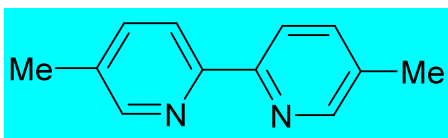
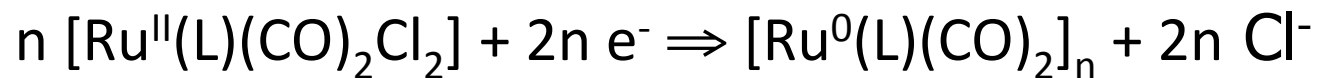


Evaluation of third axis  
 by peak at  $2\theta = 30^\circ$ :  $c = 3.0 \text{ \AA}$

Space Group Cmmm



# Electrochemically-generated thin films



(hk0) peaks  
ab plane area  
increases

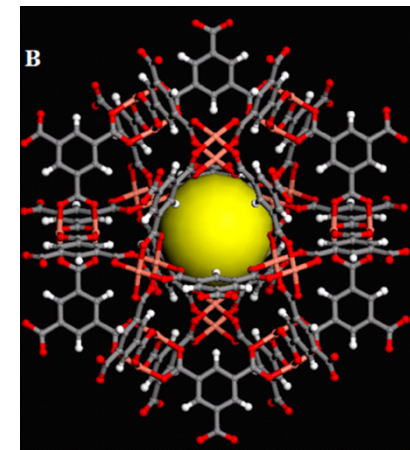
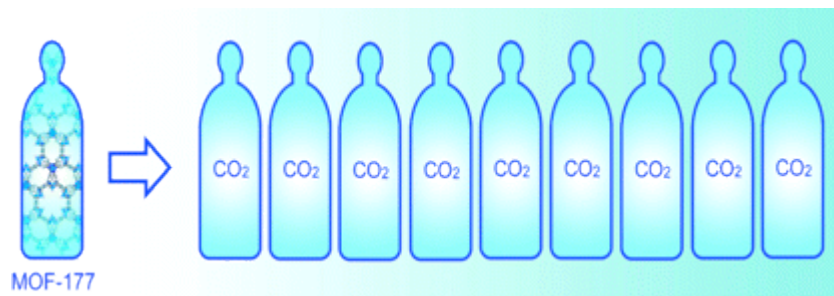
(001) peak  
Chain length:  
~ 20 monomers



# Metal Organic Frameworks

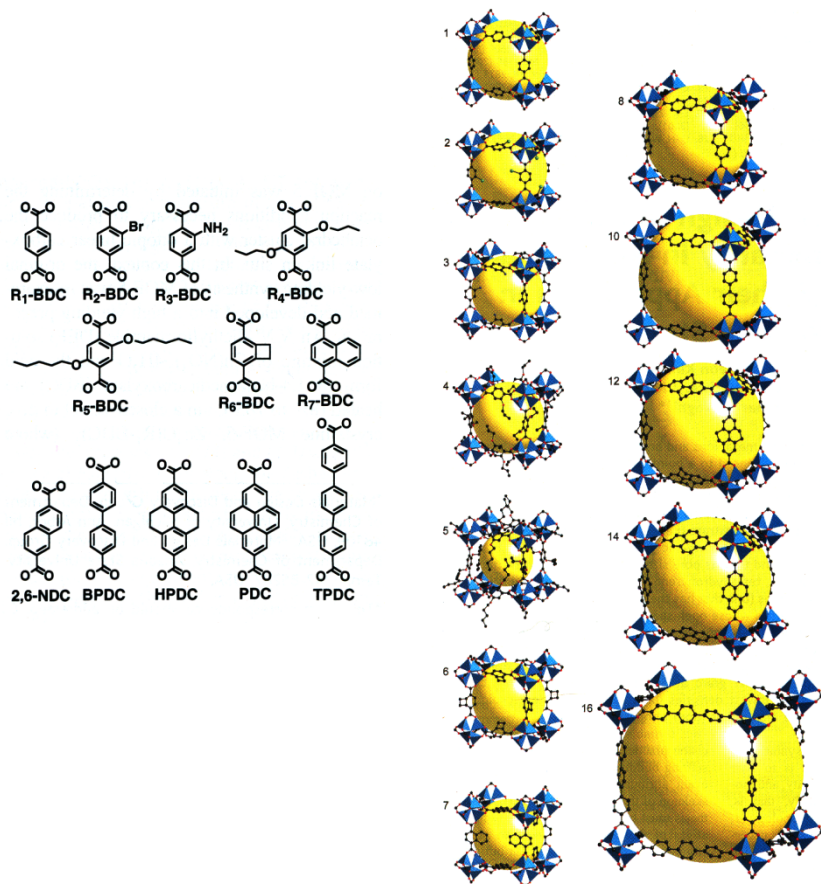
## Porous inorganic-organic hybrids

- Easily functionalized ligands and cavities
  - Prone to isorecticular chemistry
- Functional properties in gas sorption, separation, molecular recognition, drug delivery, catalysis, etc.

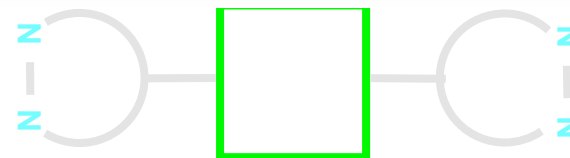


# CONTROL OF SIZE AND SHAPE OF THE PORE WALLS

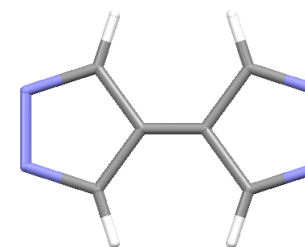
Yaghi et al. *Science*, 2002, 295, 469



# OUR APPROACH WITH NON LABILE LIGANDS

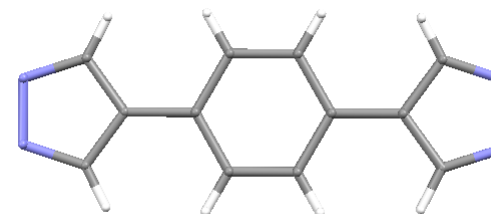


$n = 0$



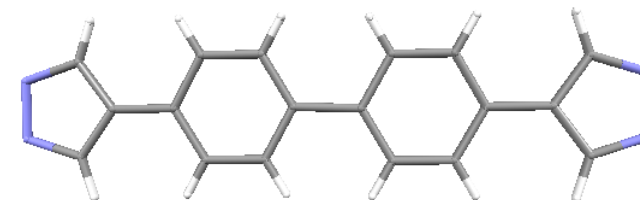
bpz

$n = 1$



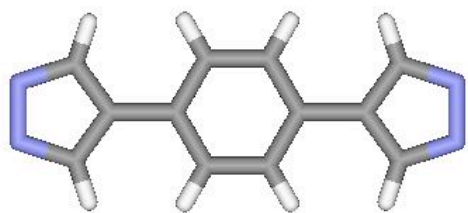
bpb

$n = 2$

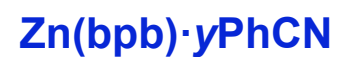
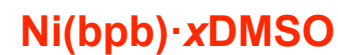
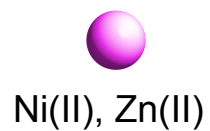


bfpz

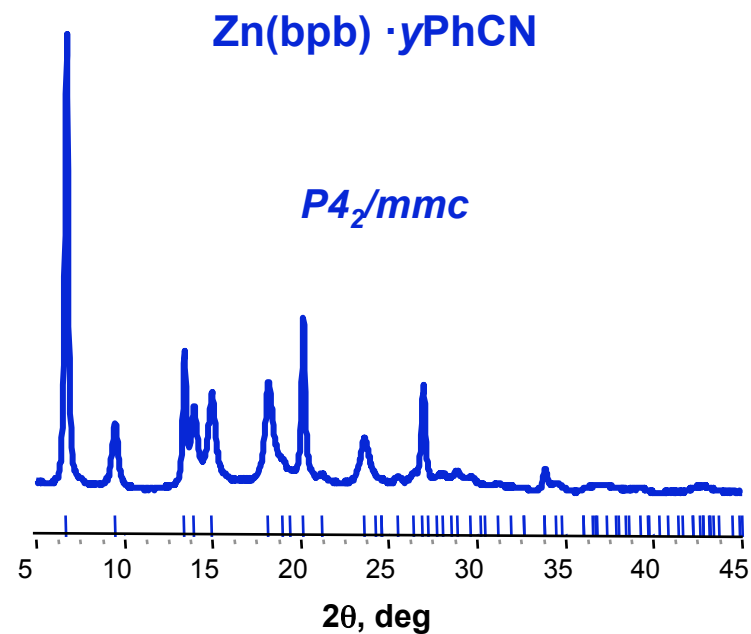
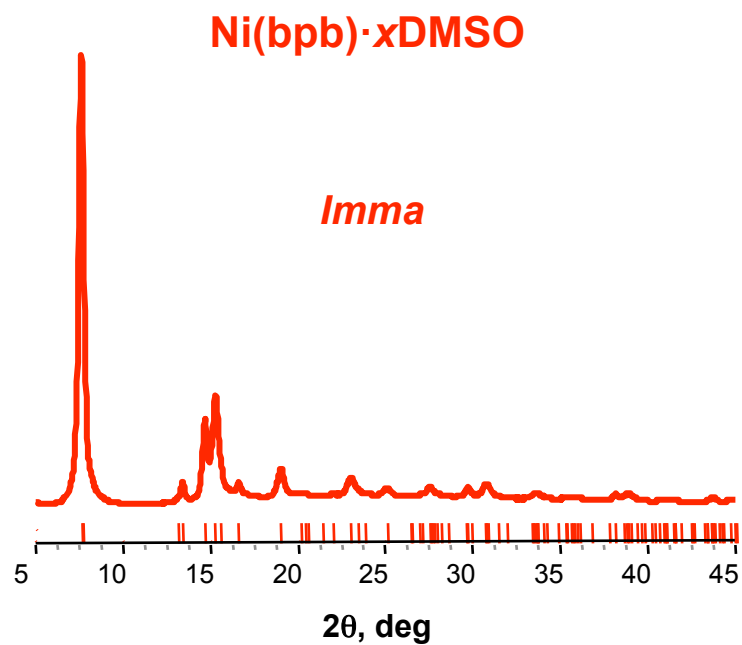
## BPB-BASED MOF'S: THE NICKEL AND ZINC DERIVATIVES

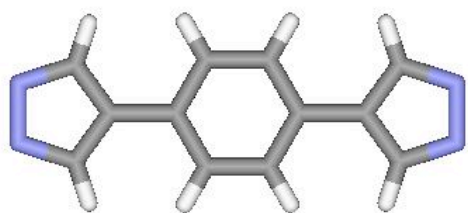


bpb

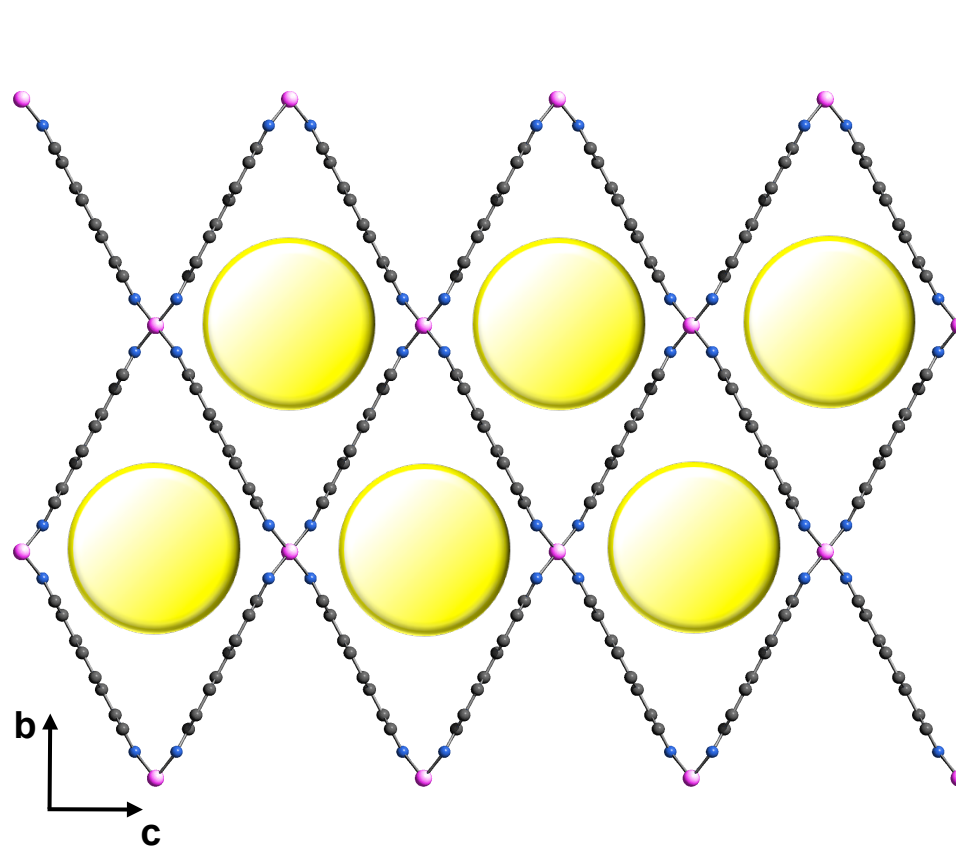
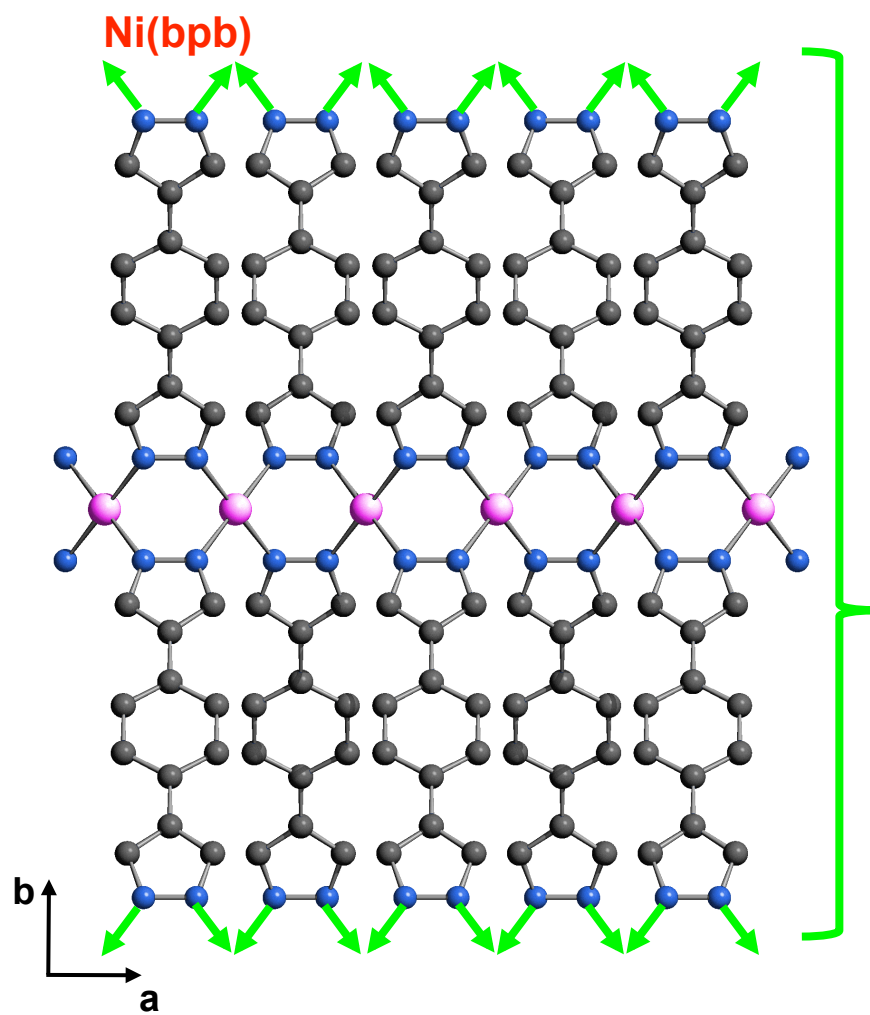
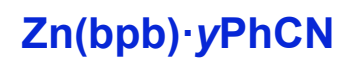
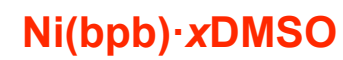
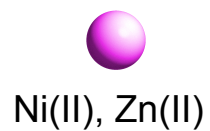


microcrystalline powders

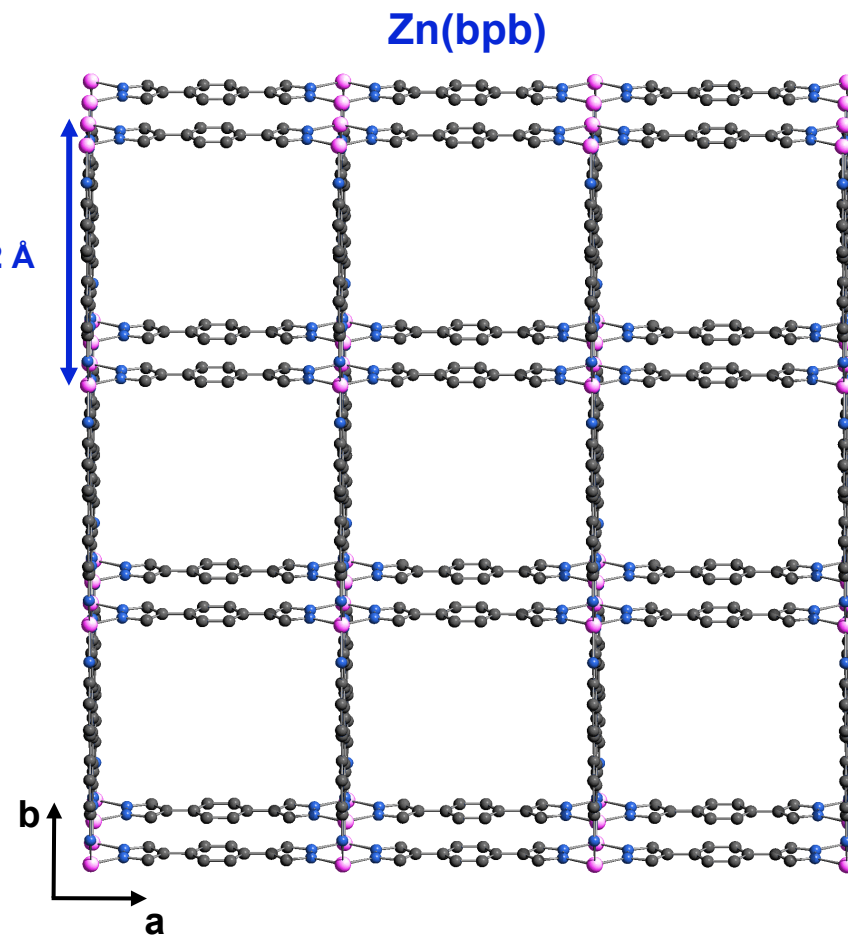
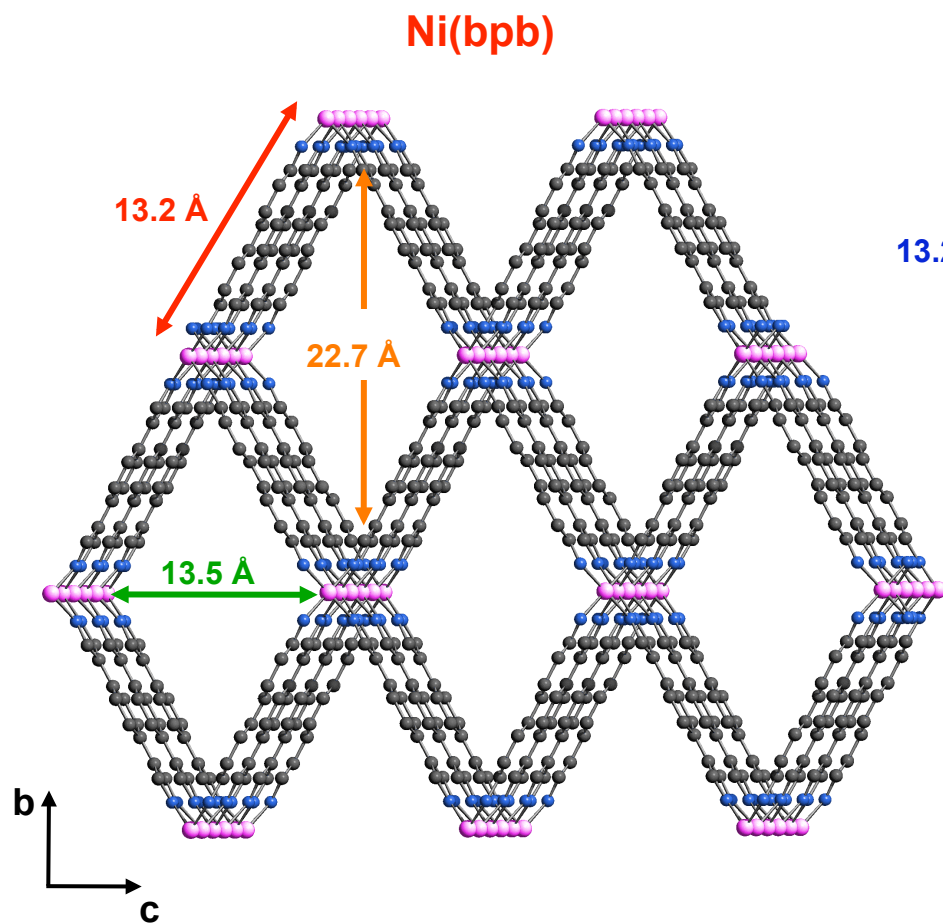




bpb



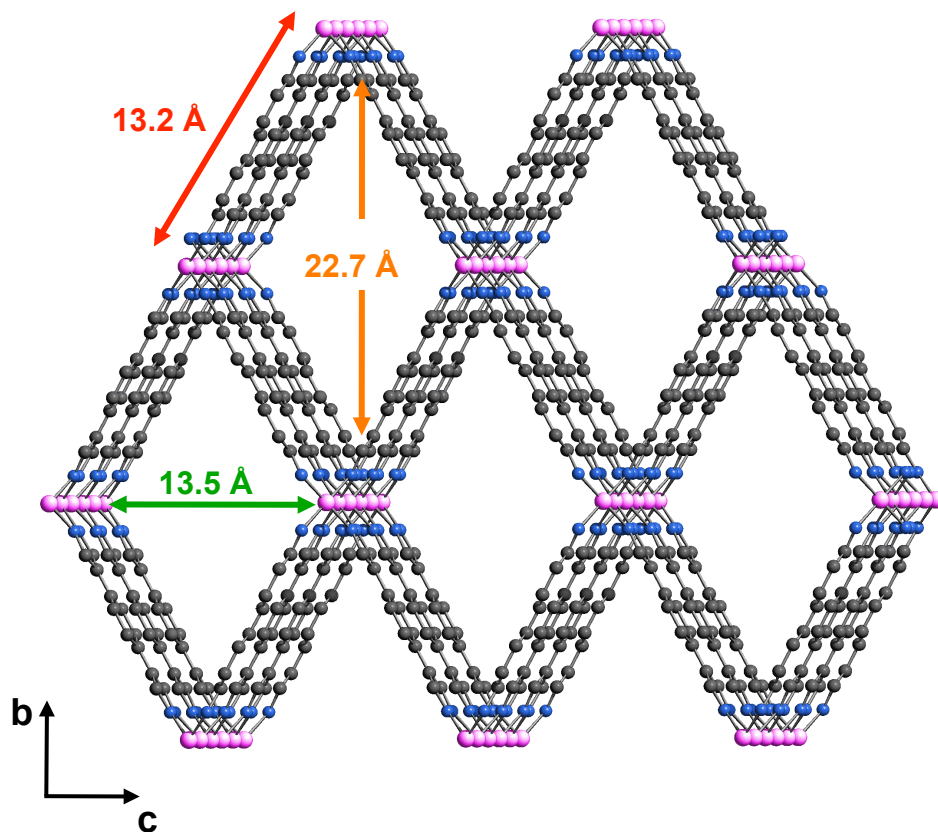
H atoms omitted for clarity



	$\rho$ , g cm <sup>-3</sup>	Void %
<b>Ni(bpb)</b>	0.86	57
<b>Zn(bpb)</b>	0.71	65

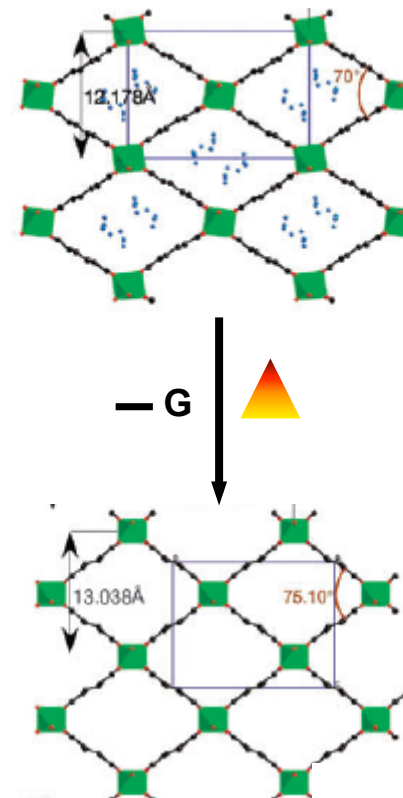
H atoms omitted for clarity

### Ni(bpb)



### MIL-53, M(X)(BDC)xG

M = Cr, Al, Fe, Ga; X = OH, F  
BDC = benzene-1,4-dicarboxylate  
G = guest

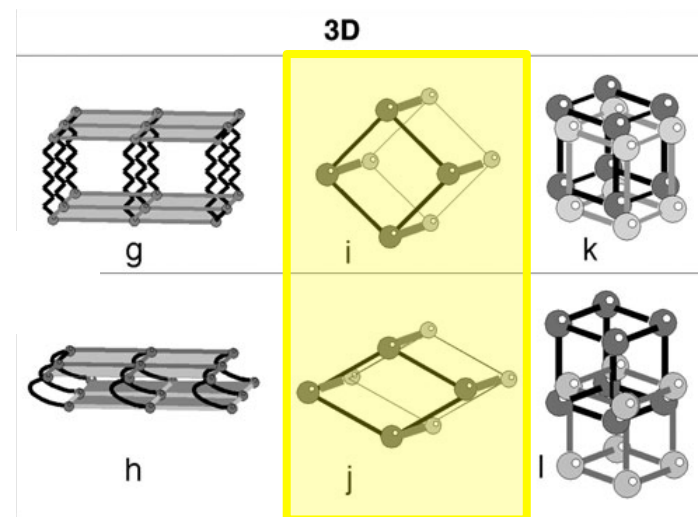
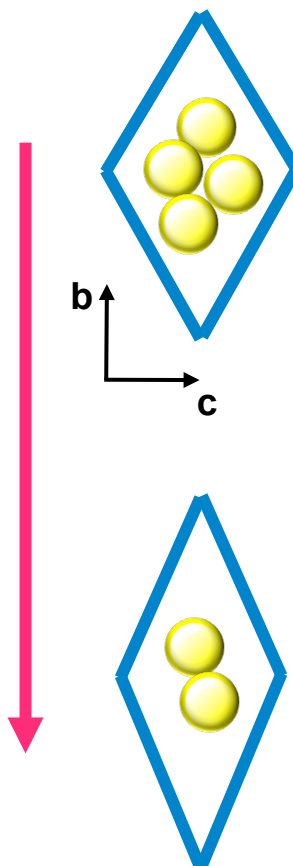


See e.g. G. Férey, C. Serre  
Chem. Soc. Rev. 2009, 38, 1380

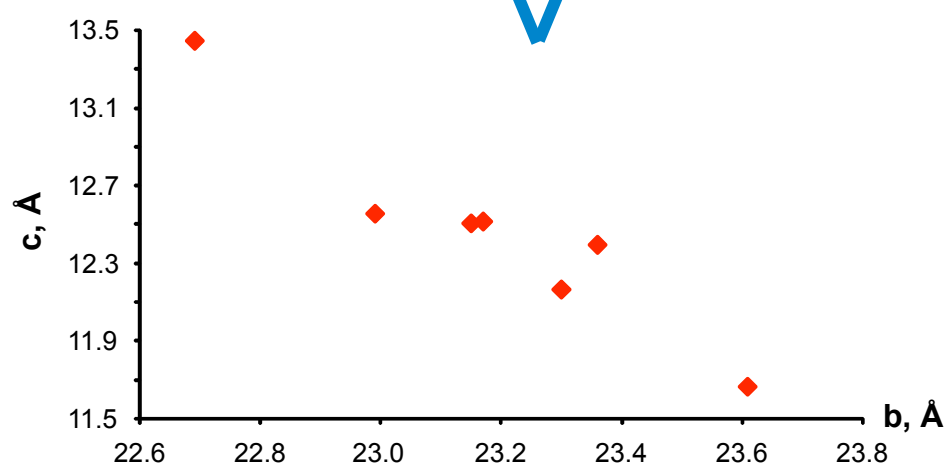
# Ni(bpb): SOLVENT-STIMULATED BREATHING

## Ni(bpb)·xH<sub>2</sub>O

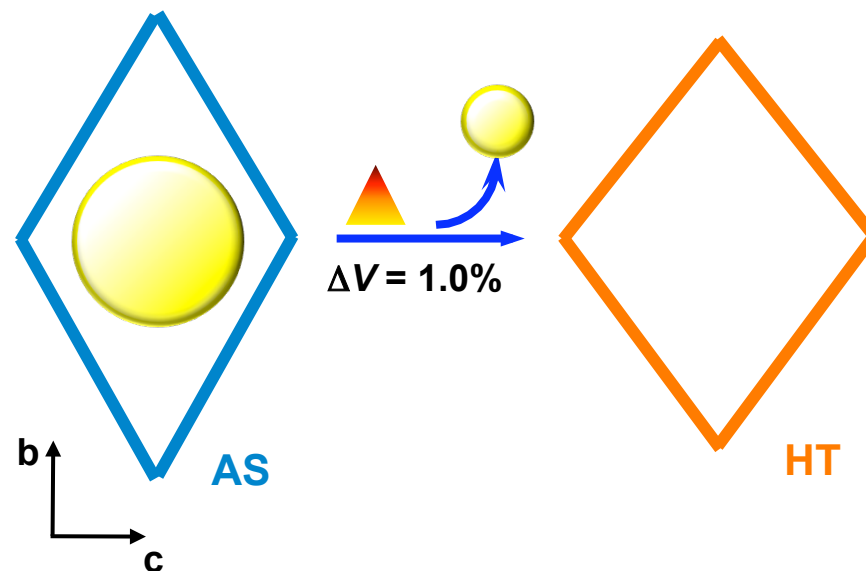
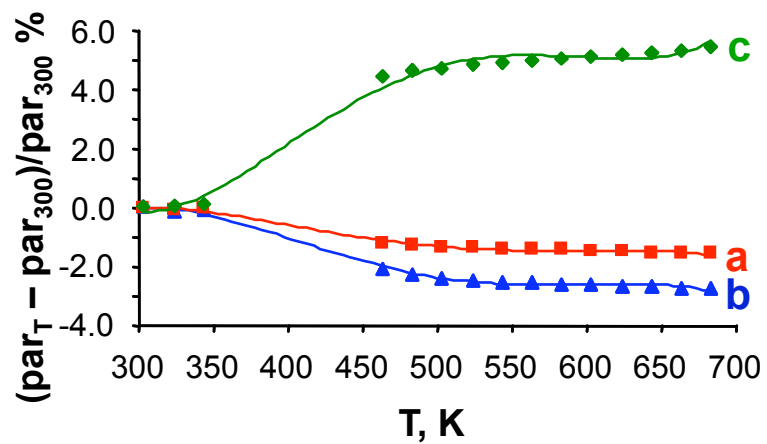
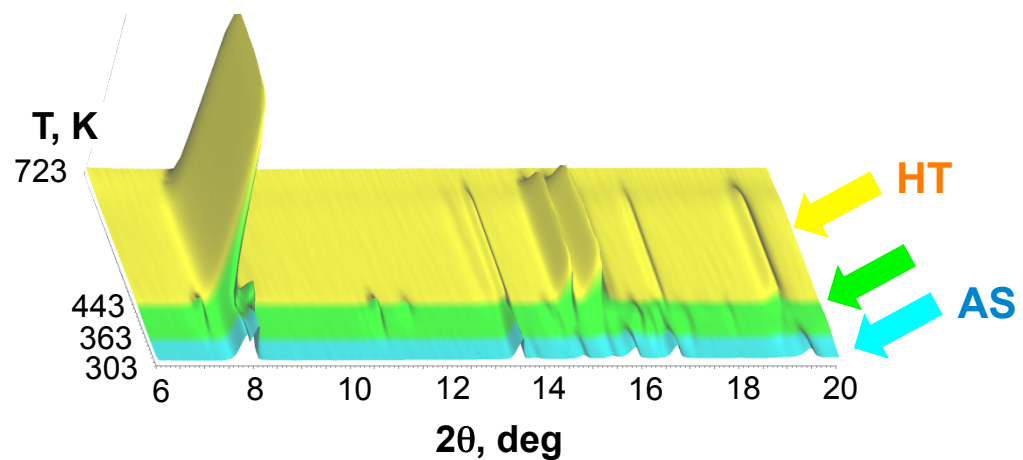
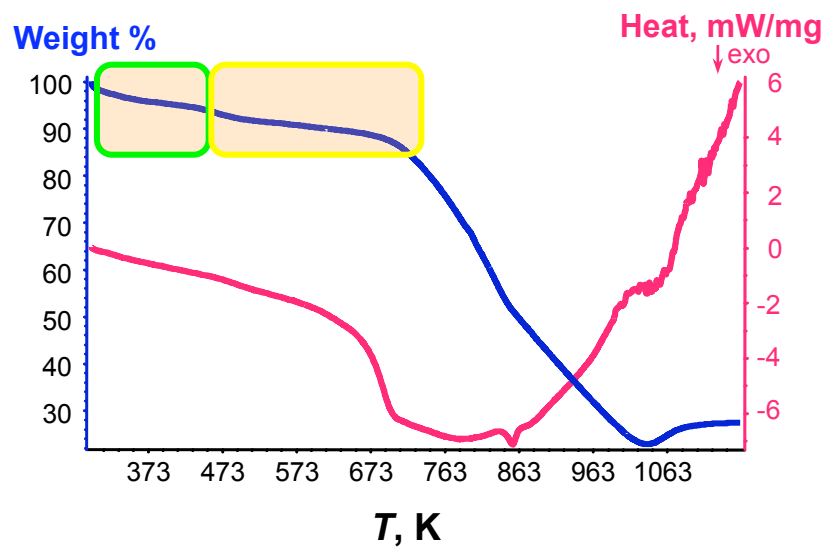
Batch	a, Å	b, Å	c, Å	V, Å <sup>3</sup>
1	6.76	22.69	13.45	2060
2	6.86	23.17	12.52	1993
3	6.78	23.15	12.51	1966
4	6.78	22.99	12.56	1958
5	6.74	23.36	12.40	1954
6	6.77	23.30	12.17	1920
7	6.66	23.61	11.67	1838



From S. Kitagawa, K. Uemura  
Chem. Soc. Rev. 2005, 34, 109

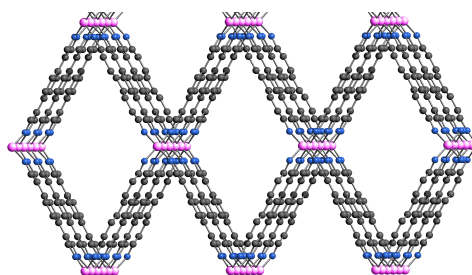
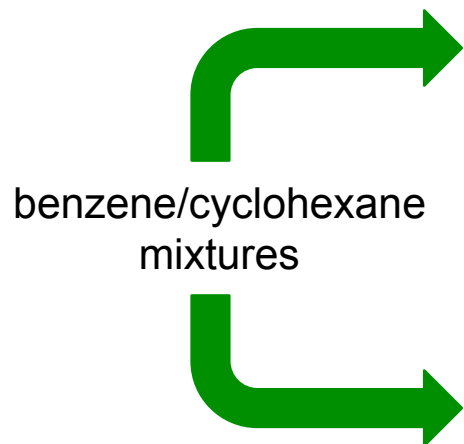
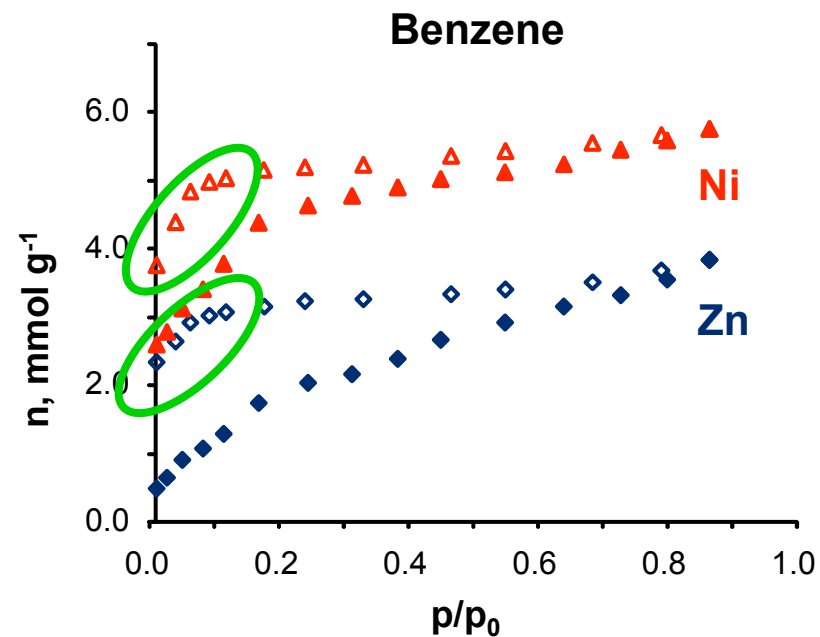
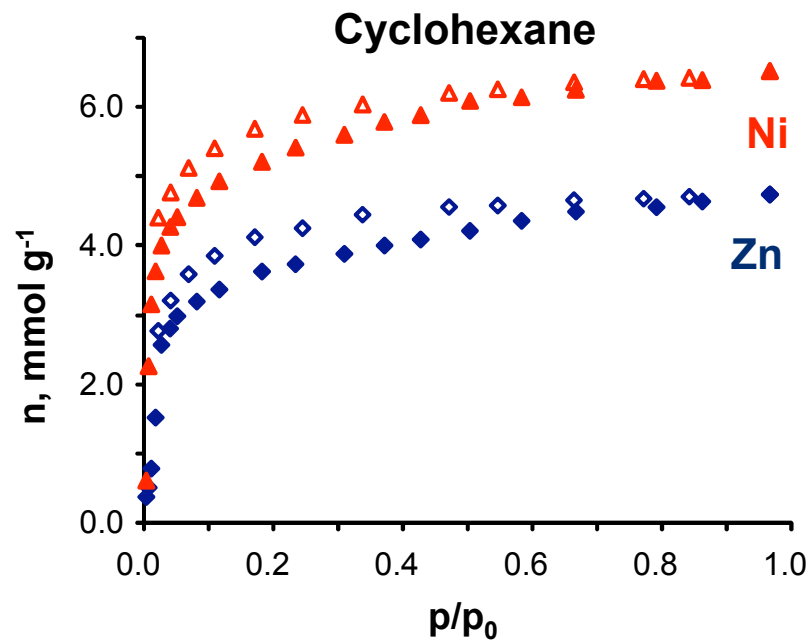


# Ni(bpb): TEMPERATURE-STIMULATED BREATHING



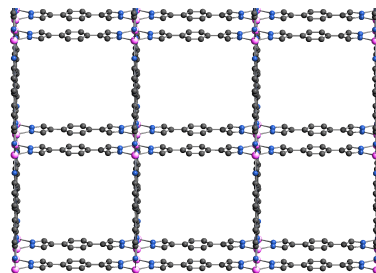


# Ni(bpb) and Zn(bpb): ORGANIC VAPOUR SEPARATION



selective benzene incorporation

cyclohexane enrichment factor 6

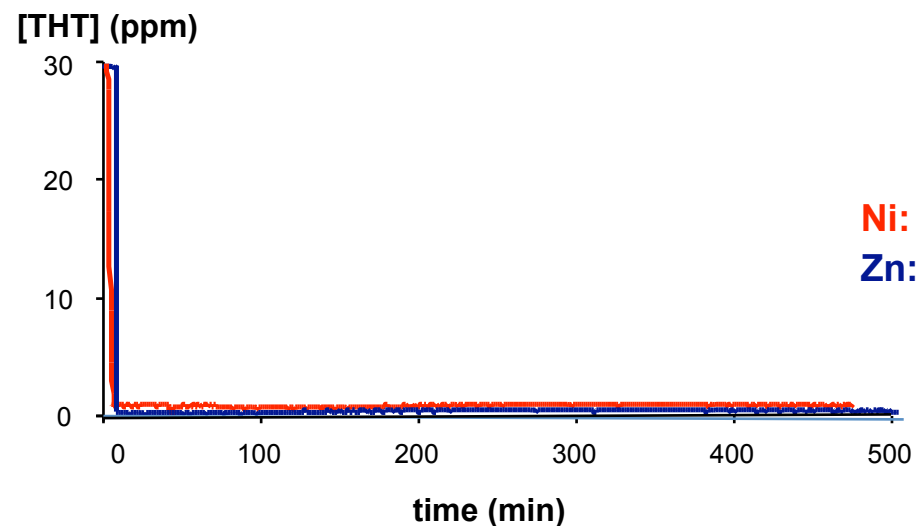


cyclohexane enrichment factor 3

## Ni(bpb) and Zn(bpb): ORGANIC VAPOUR ADSORPTION II

### EXPERIMENT A

THT in a mixture v/v of  
He:CH<sub>4</sub>:CO<sub>2</sub> = 1:2.25:1  
T = 298 K

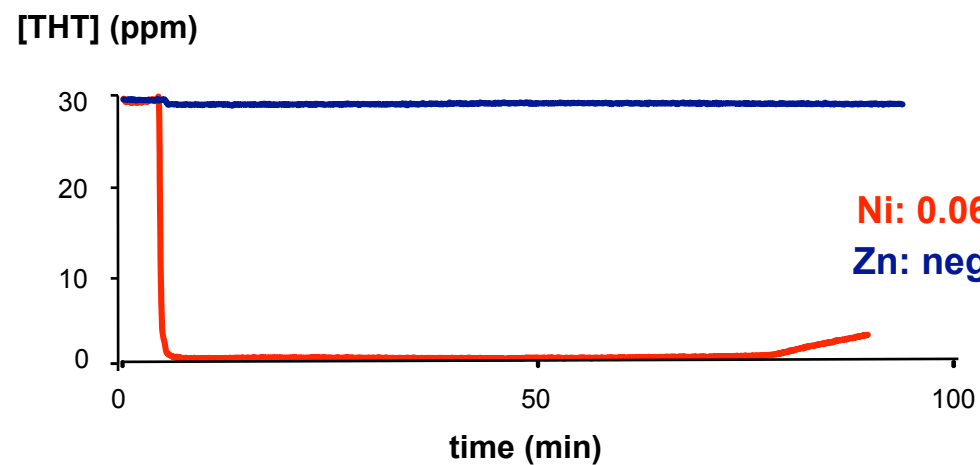


Ni: 0.30 g THT/ g MOF

Zn: 0.34 g THT/g MOF

### EXPERIMENT B

a) MOF's exposition to open  
air with 60% moisture  
b) THT in a mixture v/v of  
He:CH<sub>4</sub>:CO<sub>2</sub> = 1:2.25:1  
with 60% of moisture

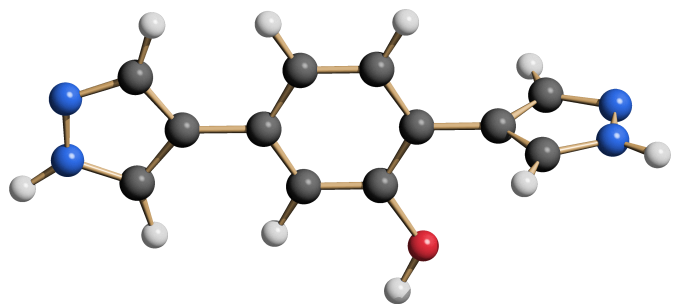


Ni: 0.06 g THT/ g MOF

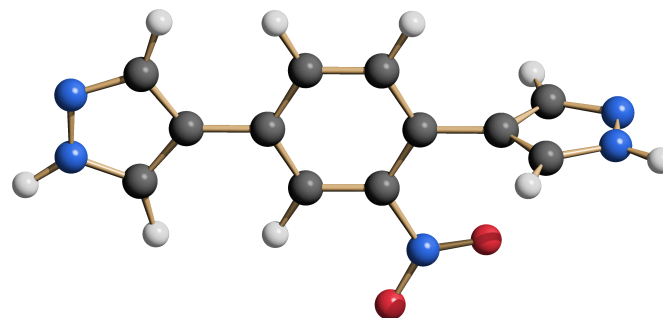
Zn: negligible

# Ligand modification

H<sub>2</sub>bpb-OH

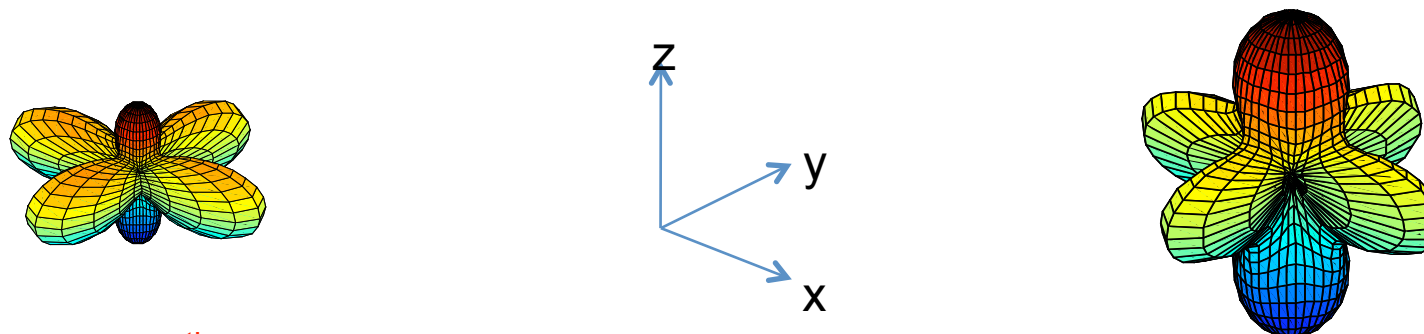
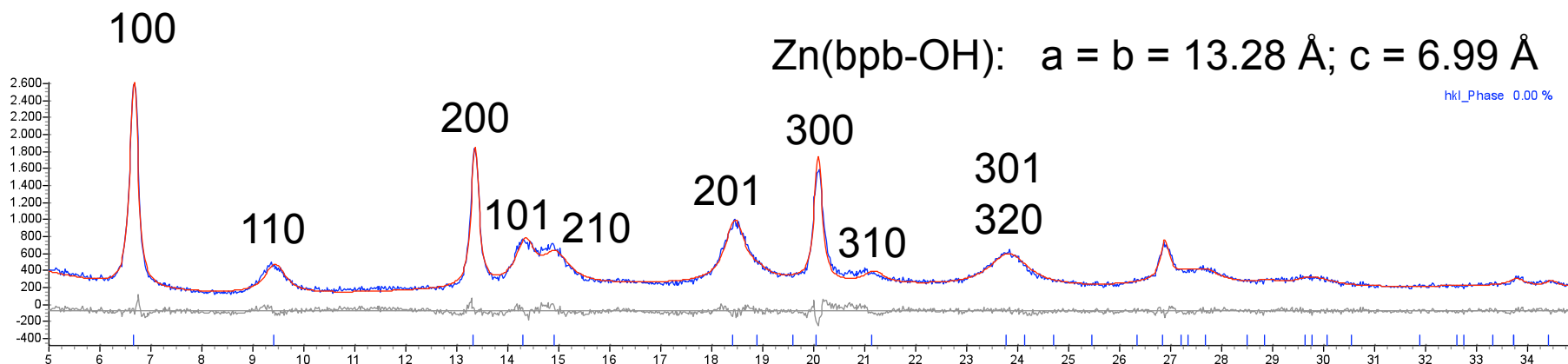


H<sub>2</sub>bpb-NO<sub>2</sub>

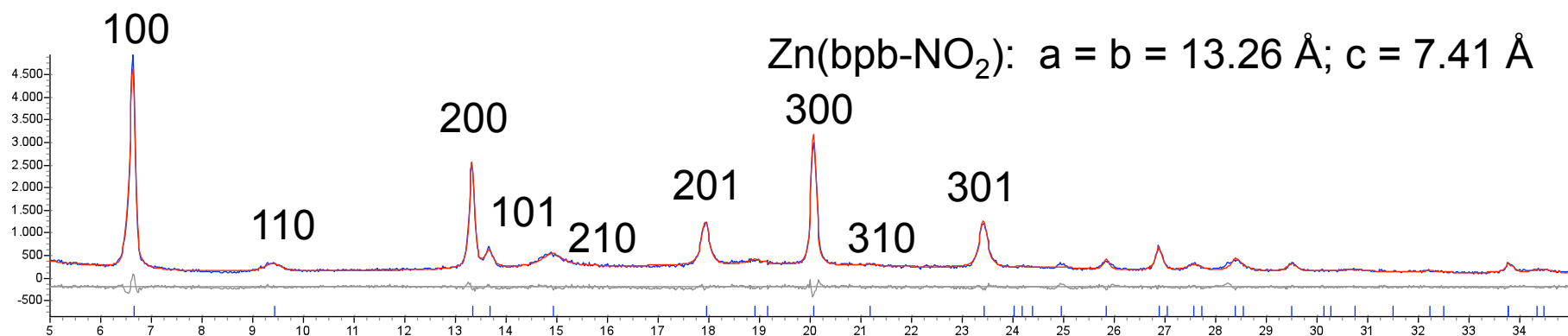


Compound	a = b, Å	c, Å	V, Å <sup>3</sup>
Zn(bpb)	13.27	7.25	1275
Zn(bpb-OH)	13.28	6.99	1233
Zn(bpb-NO <sub>2</sub> )	13.26	7.41	1303

# Paracrystalline Porous Coordination Polymers?

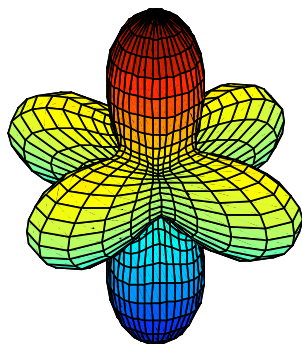
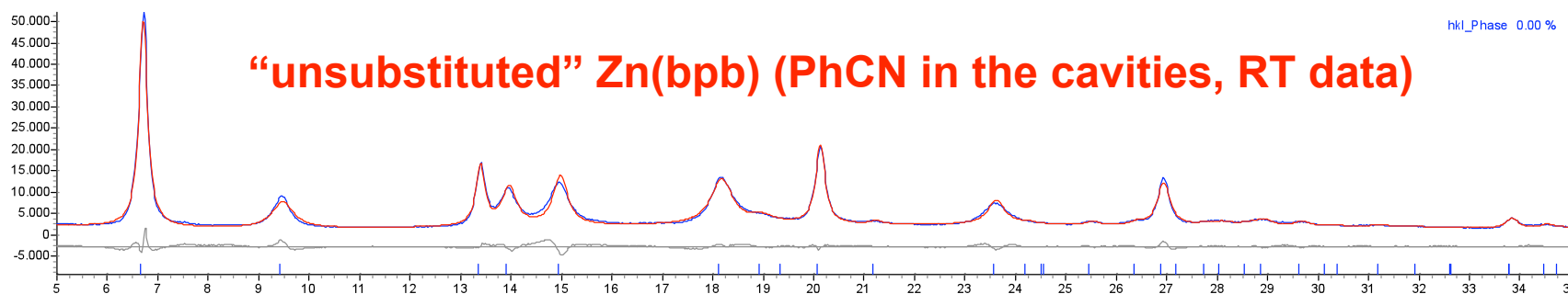


4<sup>th</sup> order spherical harmonics (4 parameters)  $\propto L$

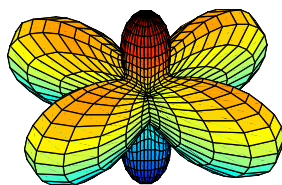


## Possible Chemical Interpretations:

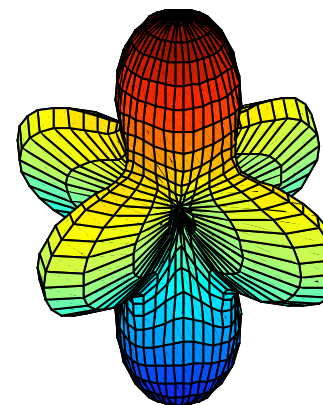
- The local asymmetry of the asymmetric bpb coordination, following the binomial distribution (Pascal's Triangle): 1,4,6,4,1
- The local inhomogeneity in the amount of solvent filling of the cavities
- Other (still unknown) reasons?



Zn(bpb)



Zn(bpb-OH)

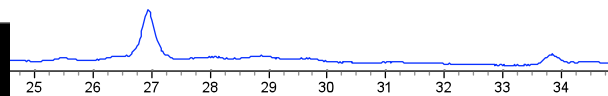
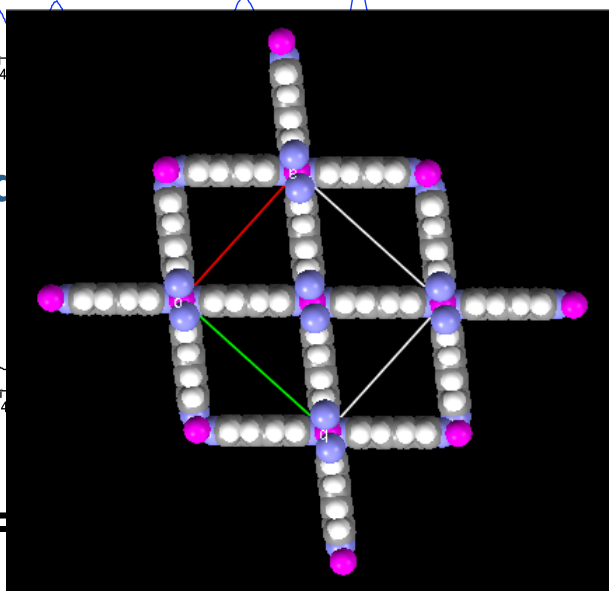
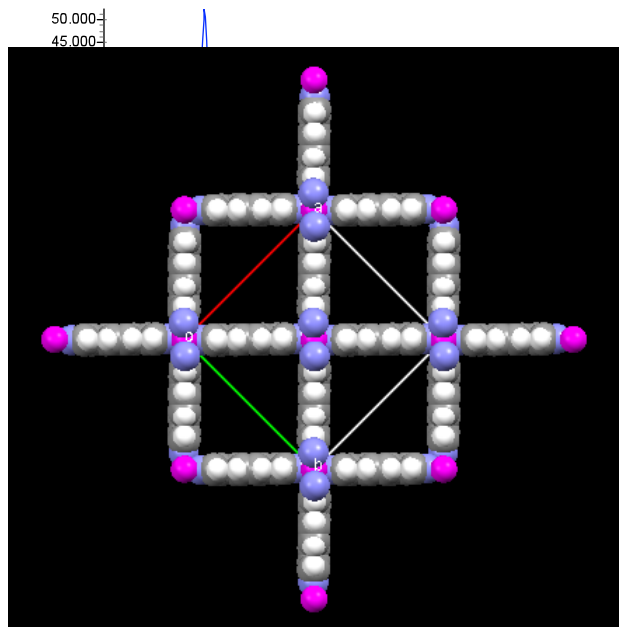


Zn(bpb-NO<sub>2</sub>)

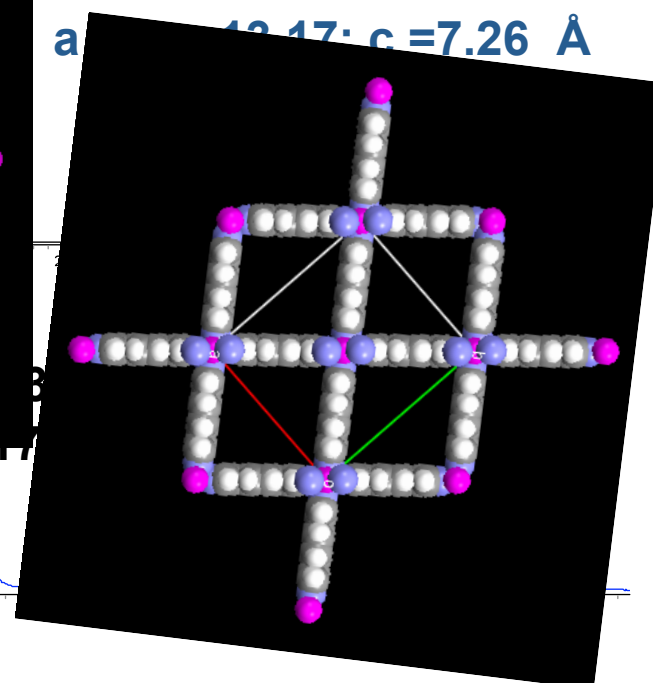
# Unsubstituted Zn(bpb):

$C_6H_5CN$  solvated:

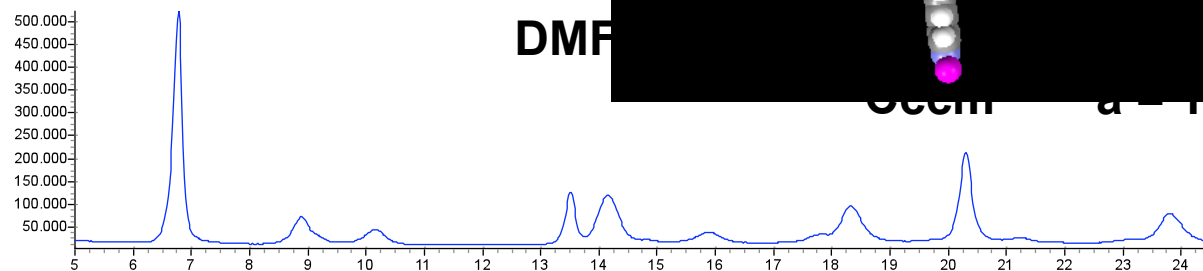
$a = b = 13.27; c = 7.25 \text{ \AA}$



$a = 13.17; c = 7.26 \text{ \AA}$



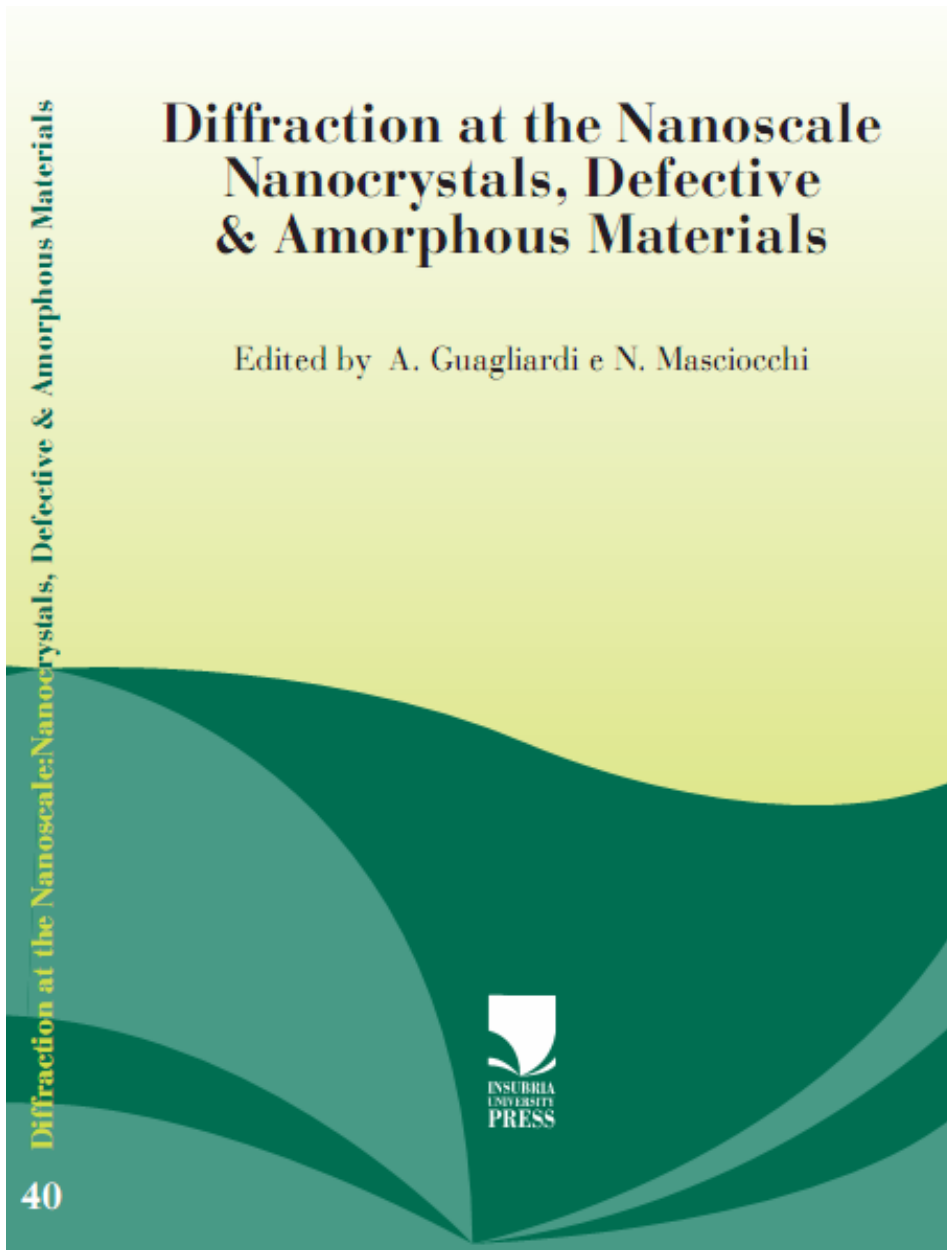
DMF



# A Common Example of a Paracrystalline Primitive Tetragonal Net



# Acknowledgments



fondazione  
c a r i p l o