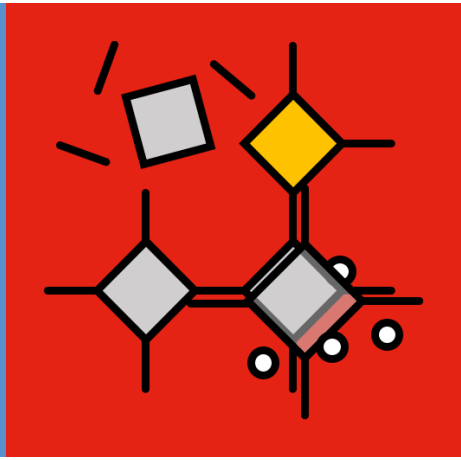
UNIVERSITY OF BIRMINGHAM

Crystallisation of framework materials

Hamish H-M Yeung

PCG Intensive Summer School 2022



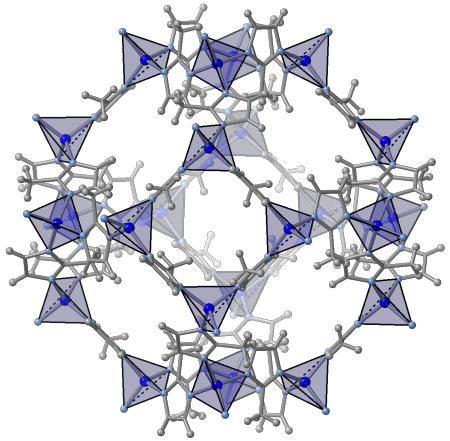
YeungGroupBham.com

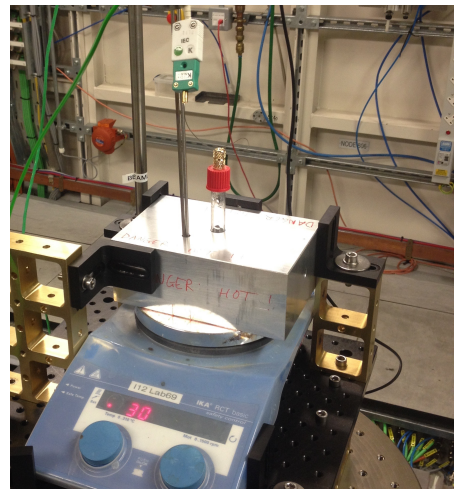
Outline

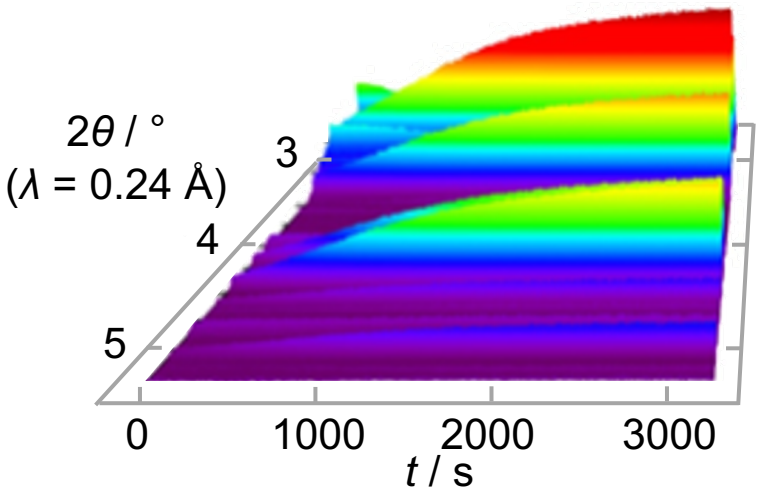
1. **Framework materials**
   - Topology + chemistry

2. **Formation studies**
   - Capabilities of *in-situ* experiments
   - Extracting quantitative information

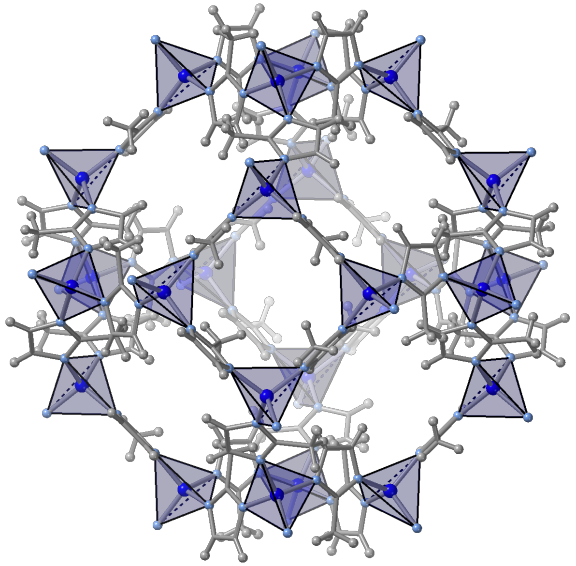
3. **Case studies**
   - Lithium tartrate polymorphism
   - ZIF-8 non-linear crystallisation
   - Zn/Cd-ZIF-8 nanoparticles



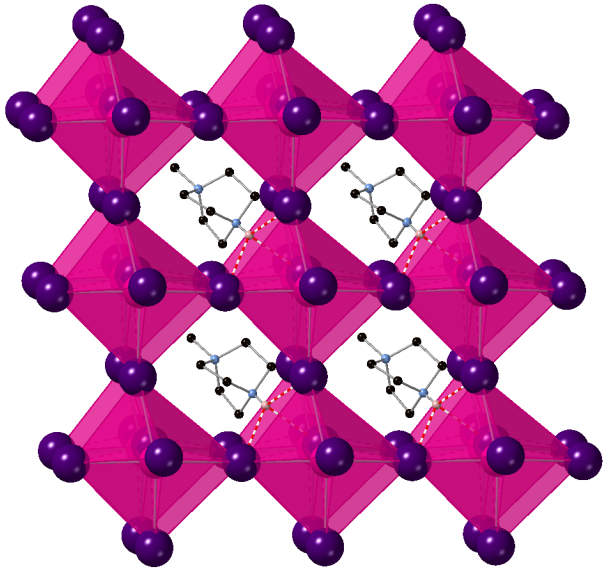




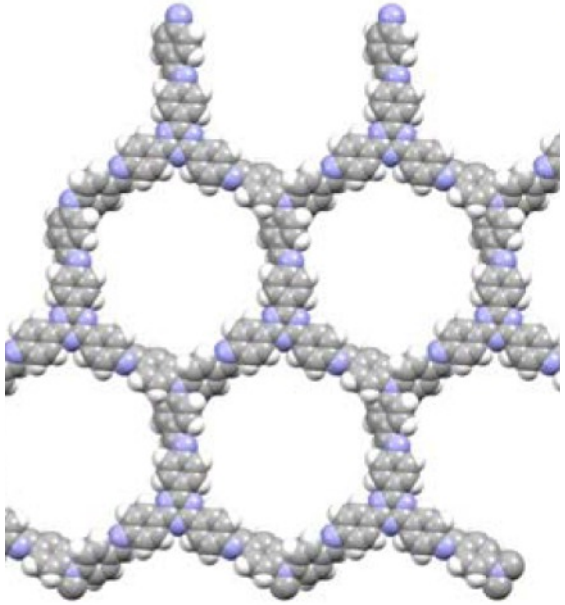
Framework materials



Metal–organic framework (MOF)



Hybrid inorganic-organic perovskite (HIOP)



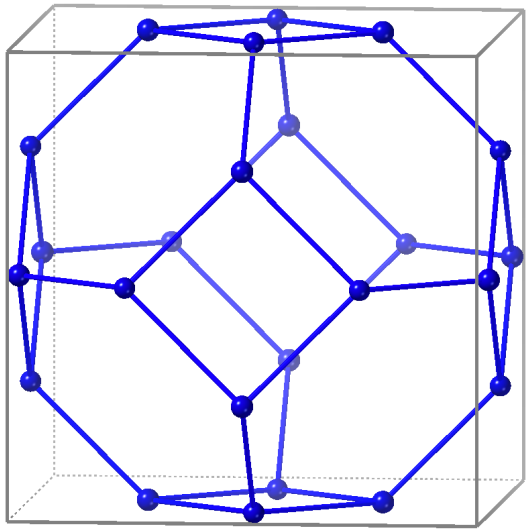
Covalent organic framework (COF)

- Magnetic, dielectric, electronic, optical and mechanical properties.
- Gas adsorption, catalytic, sensing, guest-dependent properties.
- Plenty more!

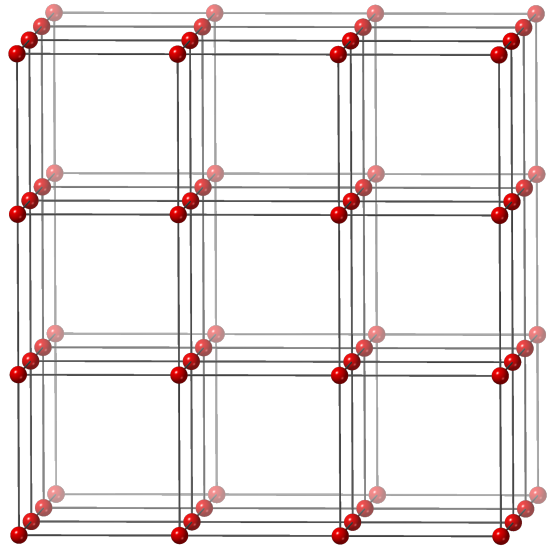
[COF figures] Adapted from R. Luo *et al.*, *Nat. Commun.* **2021**, *12*, 6808.

Net topology

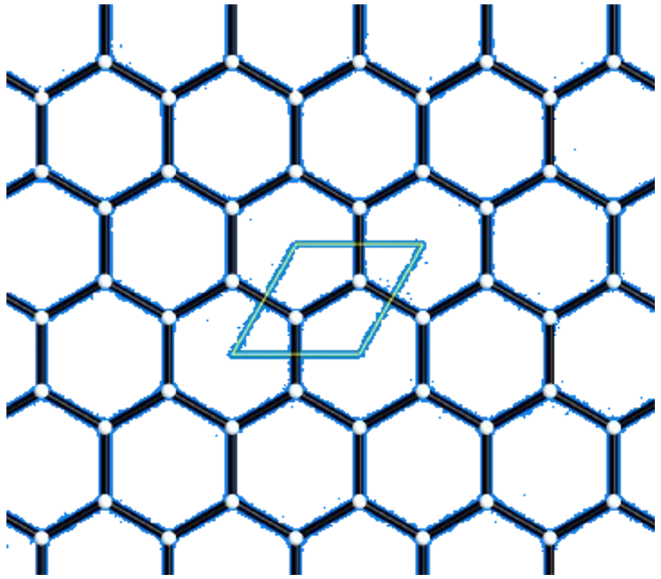
vertices (nodes) + edges (linkers)



Metal–organic framework (MOF)



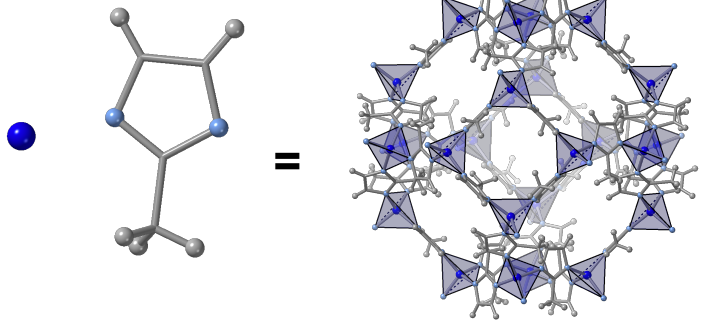
Hybrid inorganic-organic perovskite (HIOP)



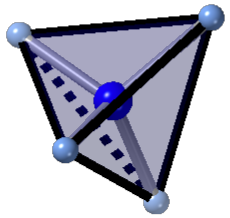
Covalent organic framework (COF)

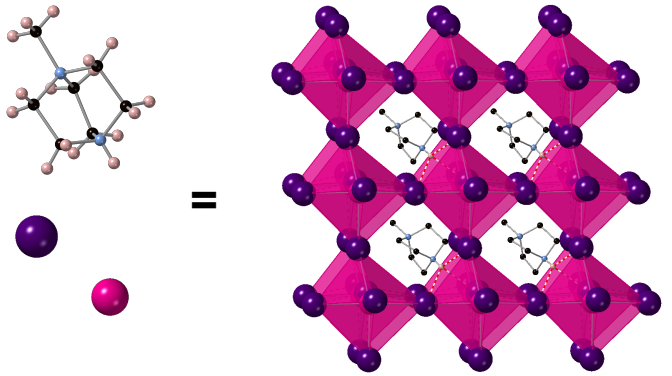
- Topology underpins dimensionality, magnetism, electronic properties etc.

Chemical building blocks

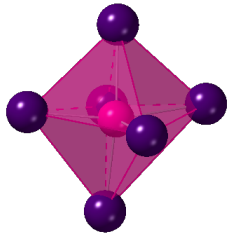


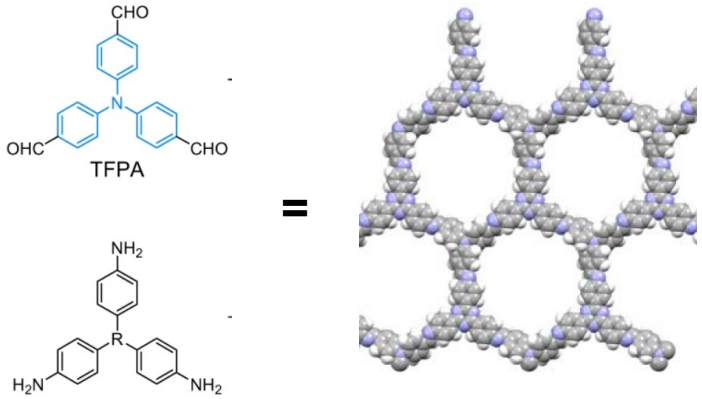
- **Metal cation**
- **Organic linker**
- Guest molecules
- Solvent molecules



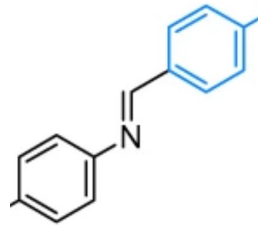


- **Metal cation**
- **Inorganic anion**
- **Organic cation** (extra-framework)



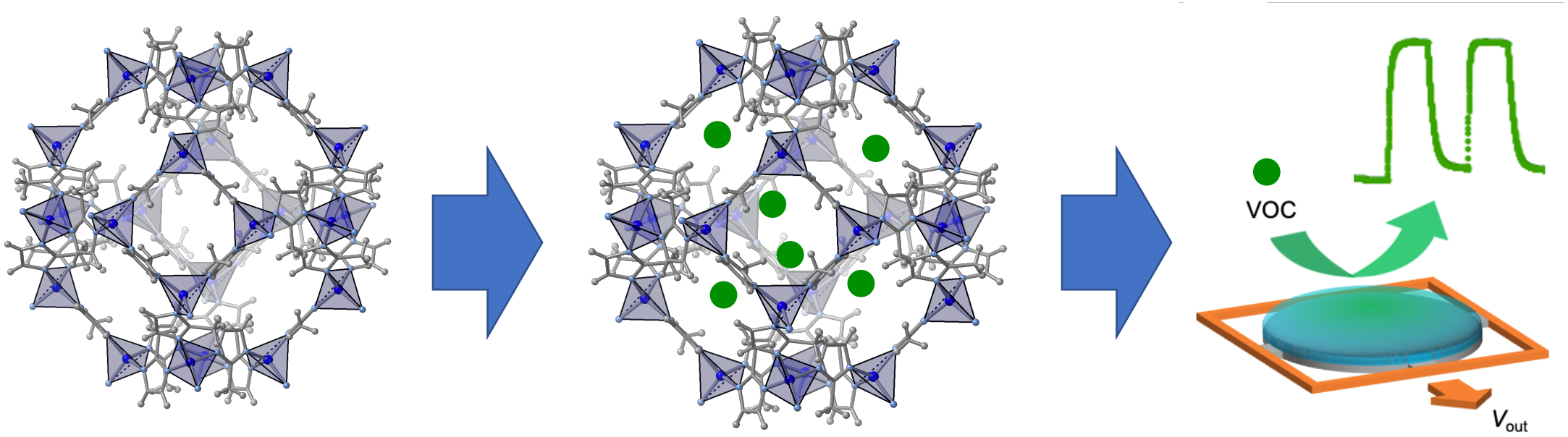


- **Organic monomers**
- Guest molecules
- Solvent molecules



- Interactions between components are key to structure formation.
- Energy scale and dynamics of the interactions determine feasible synthesis conditions.

Structure – property – application



Metal–organic framework (MOF)

Gas sorption-induced strain

Gas sensing

- Framework structure and properties can be tuned *via* building block substitution.

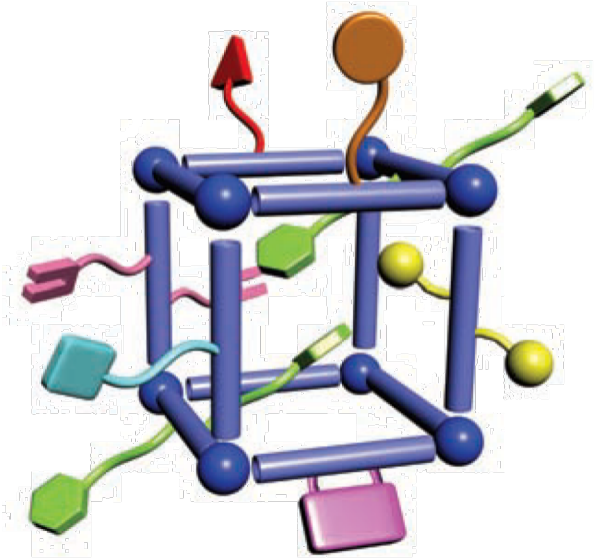
Hamish H.-M. Yeung, G. Yoshikawa, K. Minami, K. Shiba, *J. Mater. Chem. A.* **2020**, *8*, 18007–18014.

Why study formation?

Control over synthesis

- Phase purity
- Reproducibility
- Scale-up efficiency

Materials design & discovery



- Particle size
- Local structure
- Rational design

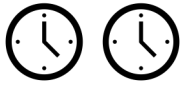
[Figure, left] SCG Chemicals, Thailand
[Figure, right] Adapted from “SpinachRuBisCO.png” under a CC BY-SA 4.0 licence, Wikipedia.org user Ericlin1337.

Framework formation

Ex-situ vs. *in-situ* investigation

	Ex-situ Analysis outside of synthesis environment	***In-situ*** Analysis during synthesis
Information	Phase behaviour Polymorphism Approximate kinetics	Meta-stable intermediates Real kinetics
Challenges	Susceptible to artefacts, e.g., phase changes	Requires modification of experiment Use of non-standard facilities Resolution can be limited

In-situ (bulk) experimental methods

	Information	Timescale
Diffraction	Long-range order	
Small-angle scattering	Scattering contrast	
Total scattering	Local structure (all sample)	
X-ray absorption spectroscopy	Local structure (element-specific)	
Nuclear magnetic resonance spectroscopy	Nuclear environments	
Other spectroscopy (IR, Raman…)	Bonding environments	
Other (pH, light scattering, colorimetry…)	various	

- Localised techniques also exist, e.g., transmission electron microscopy, atomic force microscopy.
- Other techniques can be performed in time-resolved fashion, e.g., mass spectrometry.

Quantitative kinetics

Avrami model:[1]

$$\alpha = \{1 - exp[-(k_G \times t)^{n_G}]\}$$

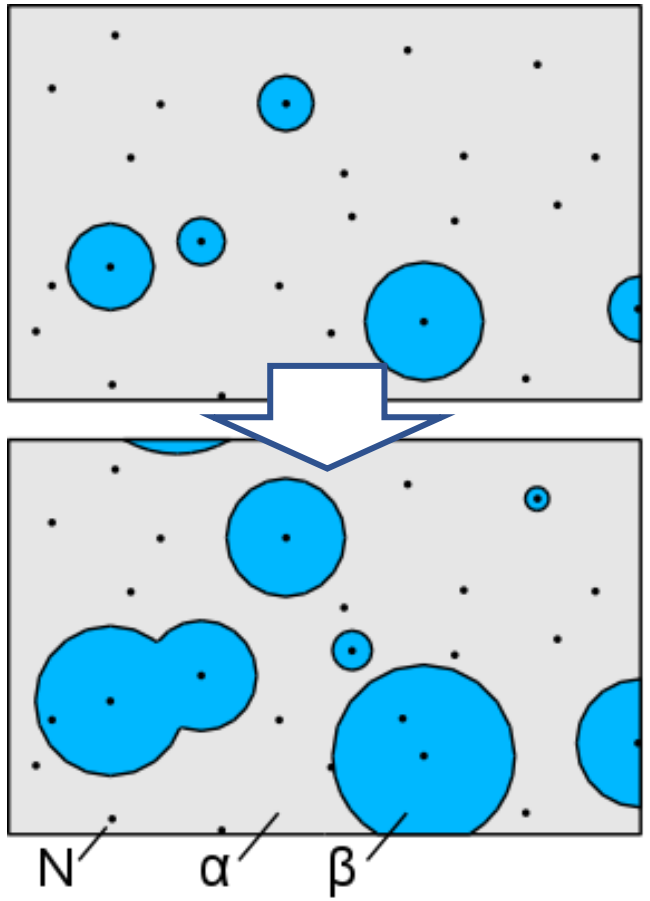
- Assumes random homogeneous nucleation of one phase in another.
- Growth rate, k_G, is independent of extent of transformation.
- Exponent, n_G, reflects the nature and dimensionality of growth.

Gualtieri model:[2]

$$\alpha = \frac{1}{1 + exp\left[\left(-\left(t - \frac{1}{k_N}\right)/b_N\right)\right]} \times \{1 - exp[-(k_G \times t)^{n_G}]\}$$

- Separates contributions from nucleation (*N*) and growth (*G*).
- Produces a nucleation probability distribution:

$$P_N = e^{-\frac{(t-1/k_N)^2}{2b^2}}$$



[1] M. Avrami, *J. Chem. Phys,* **1939**, *8*, 1103-1112; *J. Chem. Phys.*, **1940**, *8*, 212–224.
[2] A. F. Gualtieri, *Phys. Chem. Miner.* **2001**, *28*, 719–728.

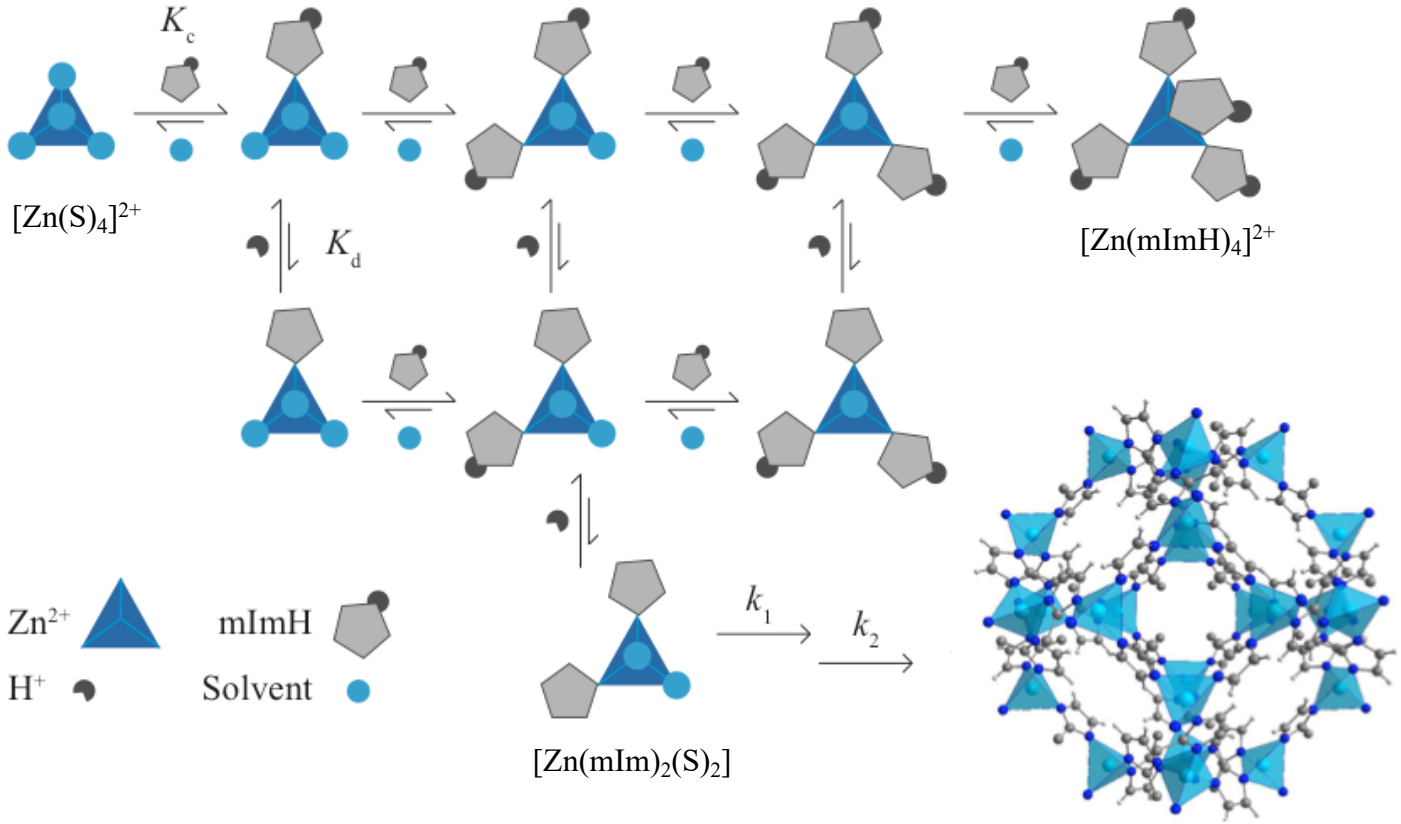
Chemical insight

Density functional theory

- Relative energies of different products.

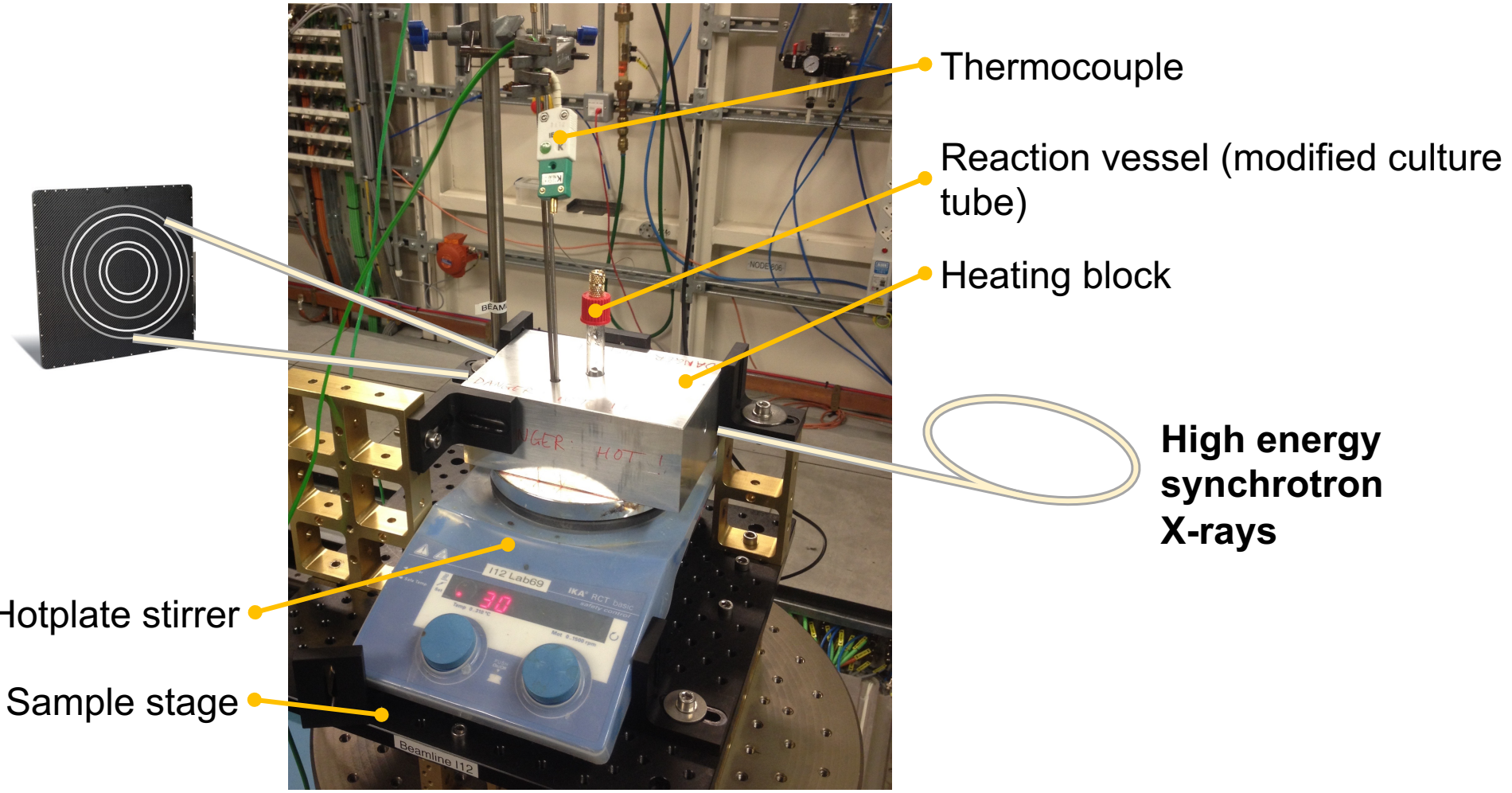
Pre-nucleation equilibrium models:[1]

- Account for changing chemistry of the reaction mixture.
- Can output variables for experimental monitoring, e.g., concentrations of individual species, yield, pH etc.
- Require validation with experimental observations.



[1] H. H.-M. Yeung, A. F. Sapnik, F. Massingberd-Mundy, M. W. Gaultois, Y. Wu, D. X. Fraser, S. Henke, R. Pallach, N. Heidenreich, O. Magdysyuk, N. T. Vo, A. L. Goodwin. *Angewandte Chemie, International Edition* **2019**, *58*, 566-571

MOF formation with *in-situ* X-ray diffraction



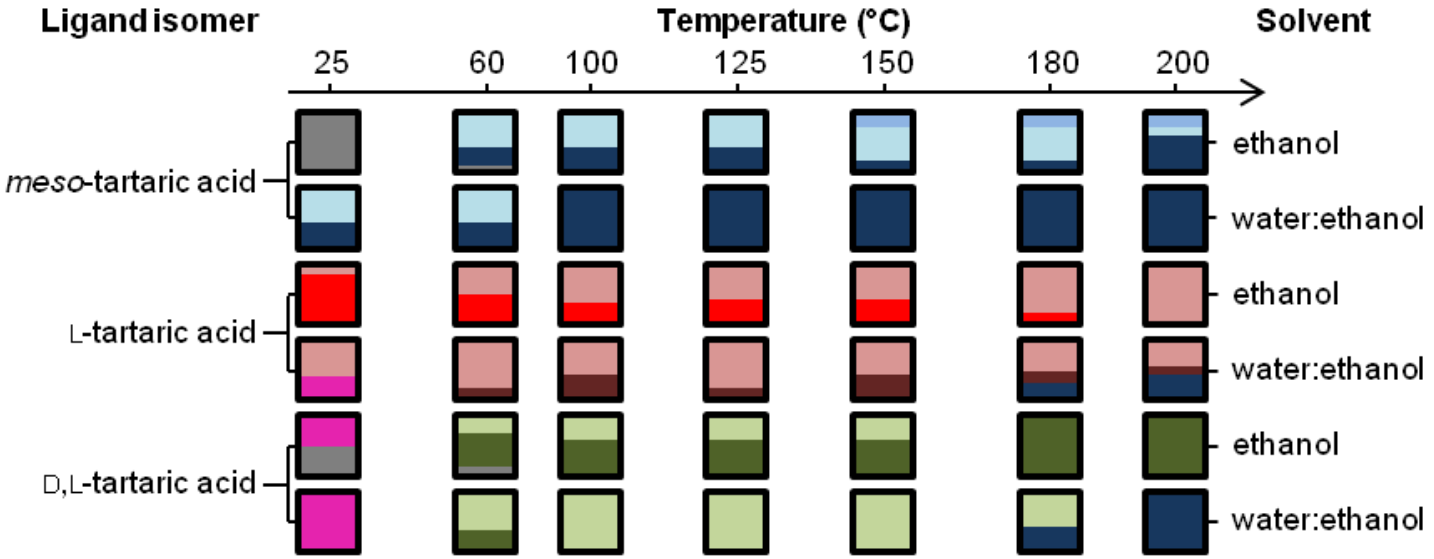
Beamline I12 - JEEP

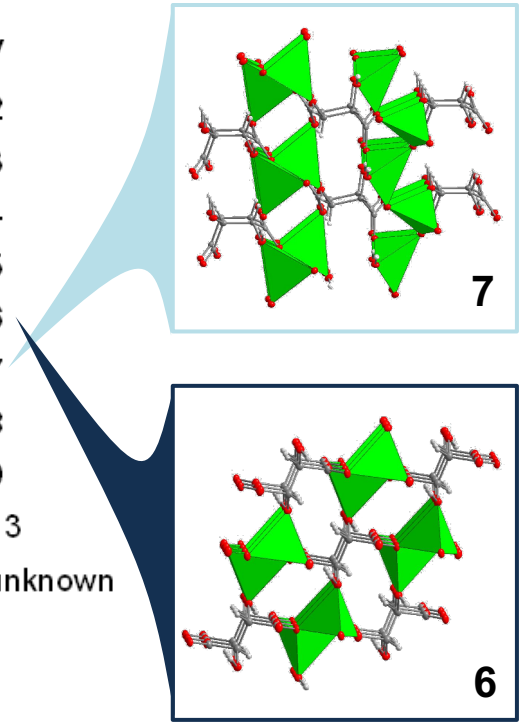
For more on Diamond: www.diamond.ac.uk/Public/How-Diamond-Works.html

Case study 1

Ex-situ: phase behaviour of lithium tartrate, $Li_2(C_4H_4O_6)$

Tony Cheetham





Kinetic?

Thermodynamic?

H. H.-M. Yeung, A. K. Cheetham, *Dalton Transactions* **2014**, *43*, 95–102.

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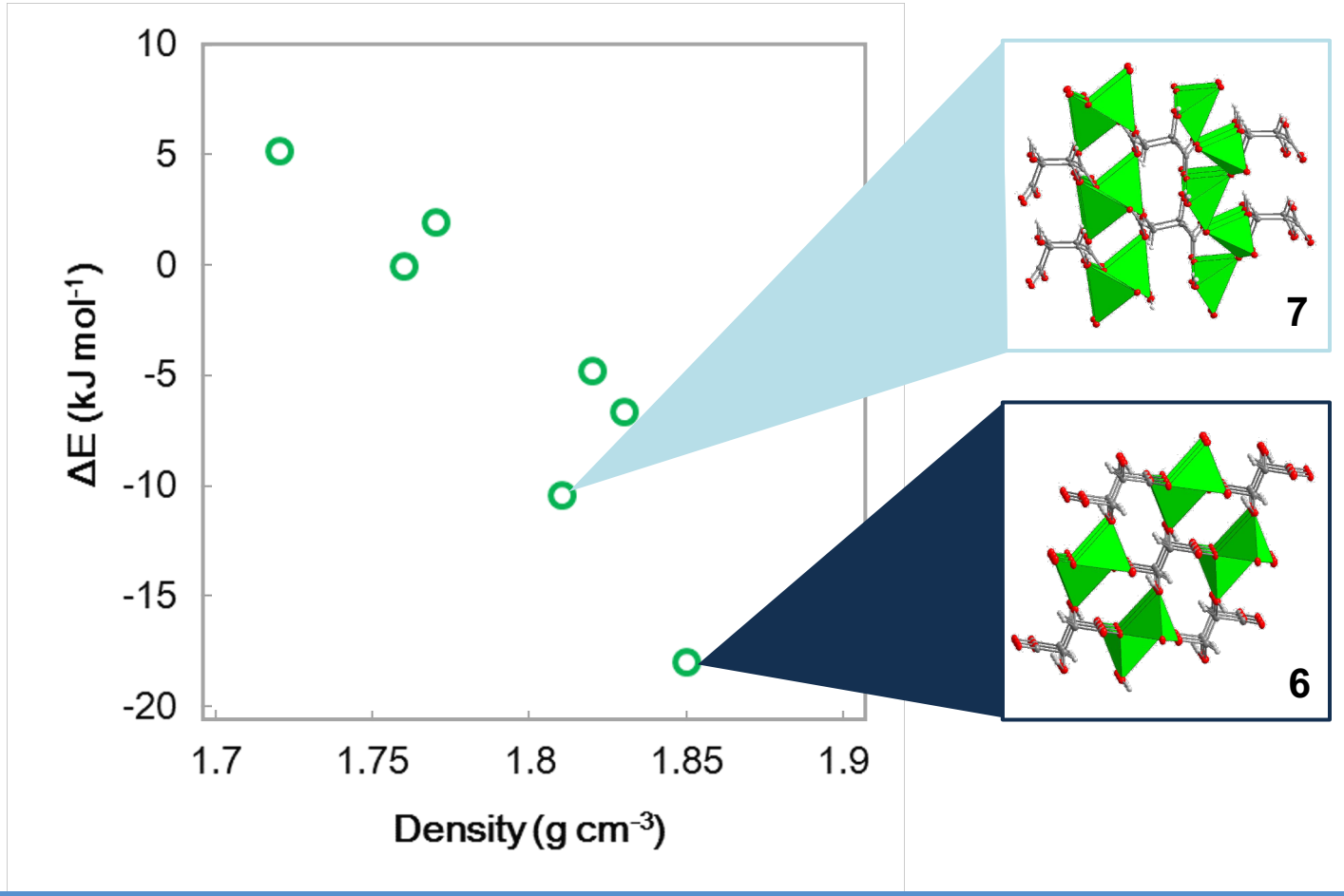
Computation: energetics of lithium tartrate, $Li_2(C_4H_4O_6)$

Monica Kosa



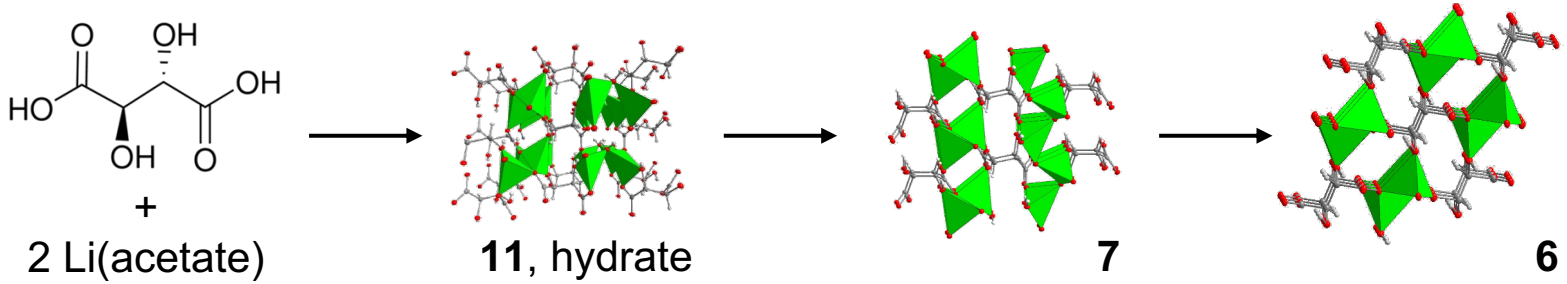
Metastable phase

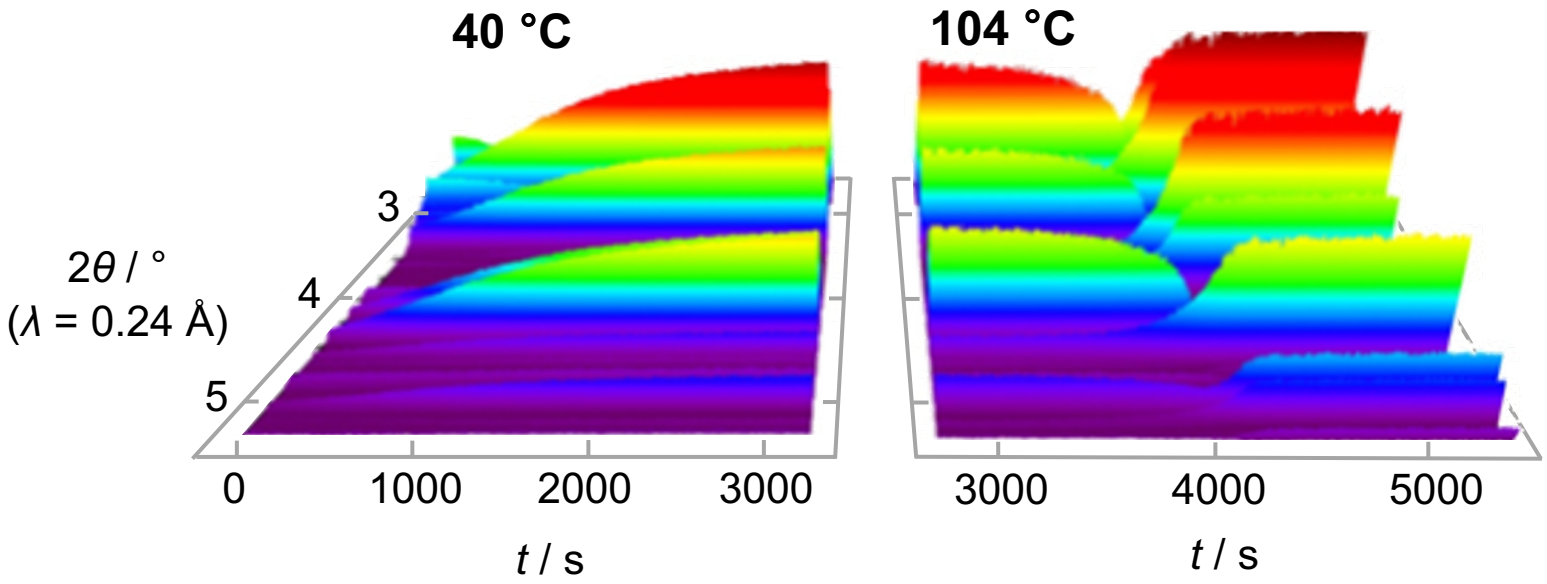
Thermodynamic product

H. H.-M. Yeung, M. Kosa, M. Parrinello, P. M. Forster, A. K. Cheetham, *Crystal Growth and Design* **2011**, *11*, 221–230.
H. H.-M. Yeung, M. Kosa, M. Parrinello, A. K. Cheetham, *Crystal Growth and Design* **2013**, *13* (8), 3705–3715.

In-situ: successive crystallisations

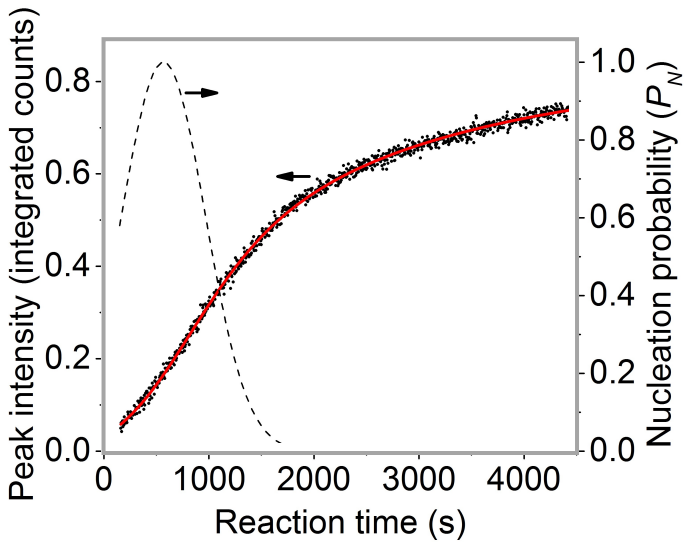
Richard Walton

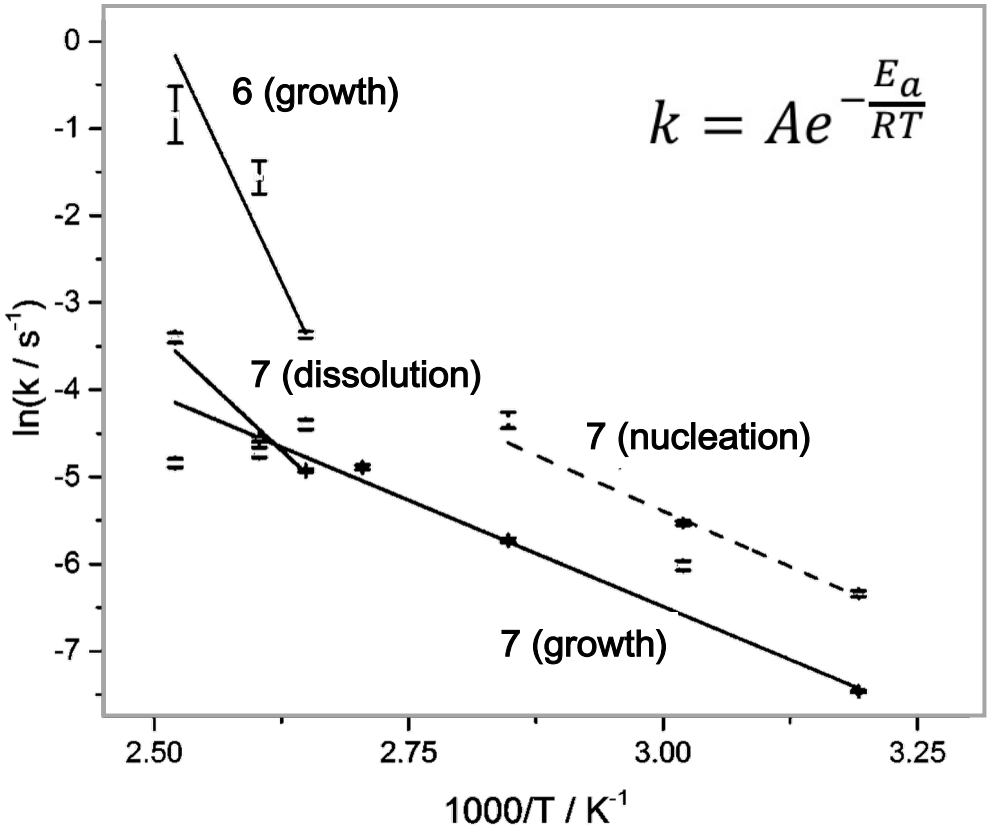




H. H.-M. Yeung, Y. Wu, S. Henke, A. K. Cheetham, D. O'Hare, R. I. Walton
Angewandte Chemie, International Edition **2016**, *55*, 2012–2016.

Kinetics



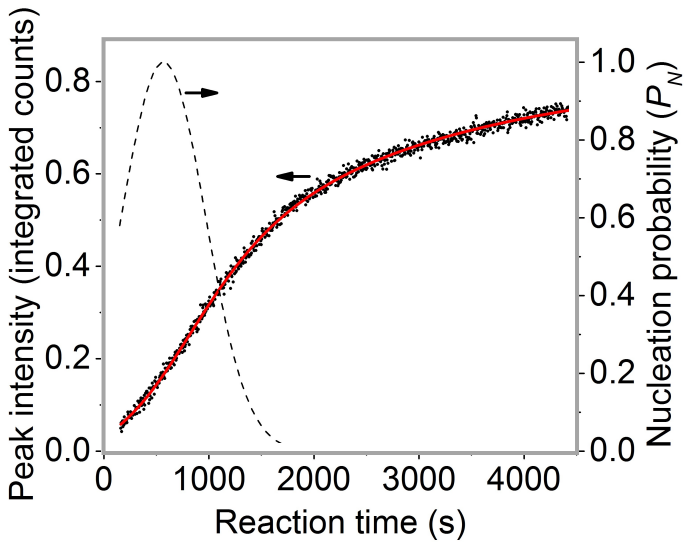


Gualtieri model fitting:

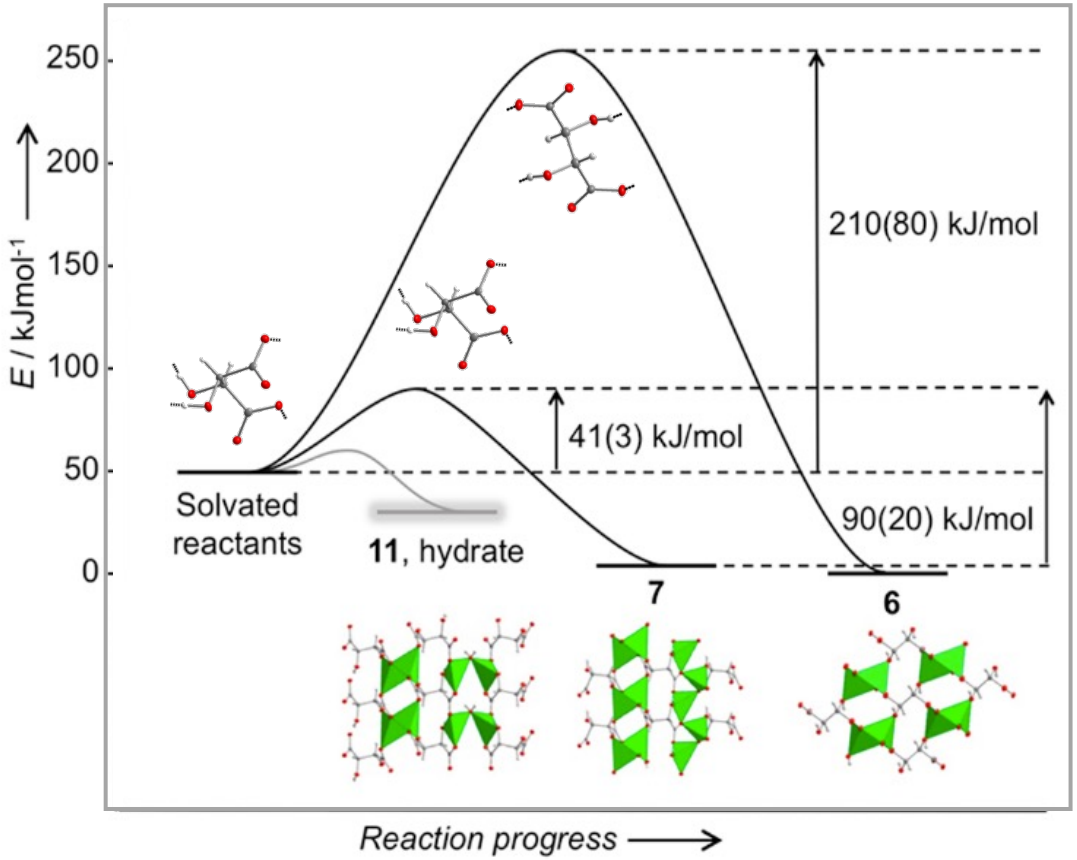
$$\alpha = \frac{1}{1 + exp\left[\left(-\left(t - \frac{1}{k_N}\right)/b_N\right)\right]} \times \{1 - exp[-(k_G \times t)^{n_G}]\}$$

H. H.-M. Yeung, Y. Wu, S. Henke, A. K. Cheetham, D. O'Hare, R. I. Walton
Angewandte Chemie, International Edition **2016**, *55*, 2012–2016.

Energy landscape



+ computed relative energies



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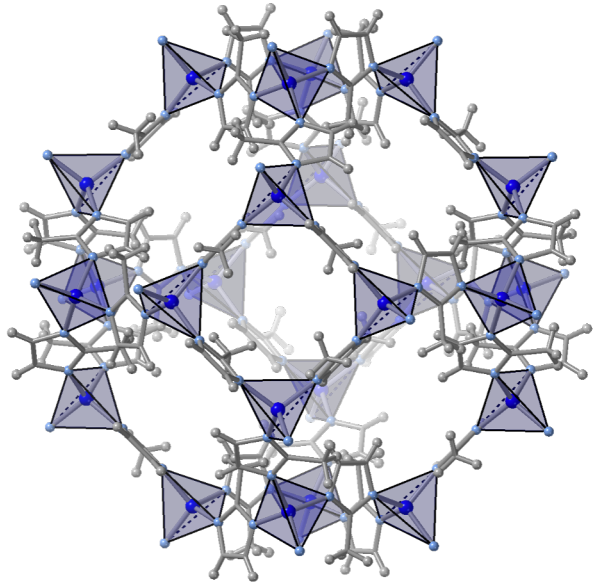
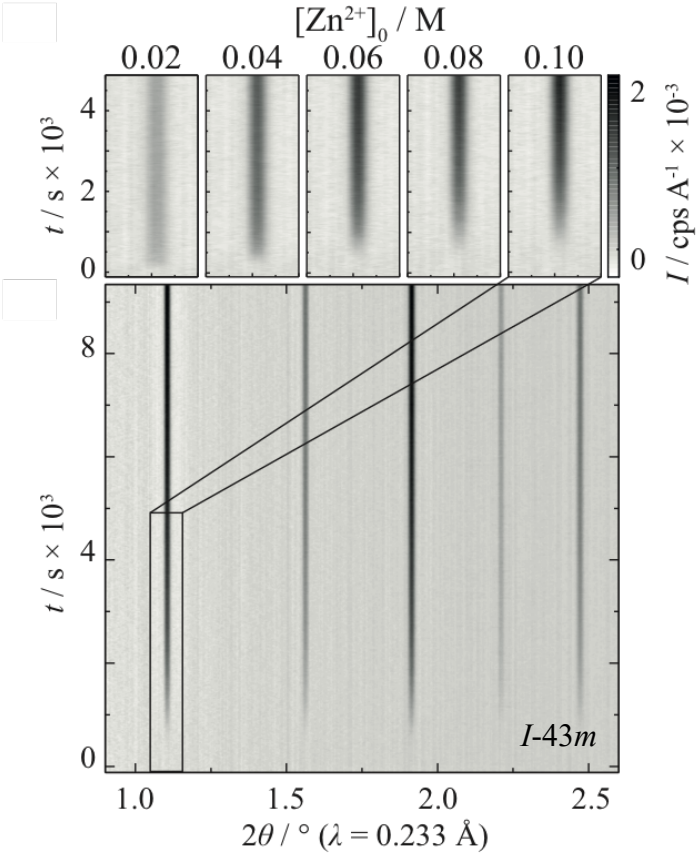
H. H.-M. Yeung, Y. Wu, S. Henke, A. K. Cheetham, D. O'Hare, R. I. Walton
Angewandte Chemie, International Edition **2016**, *55*, 2012–2016.

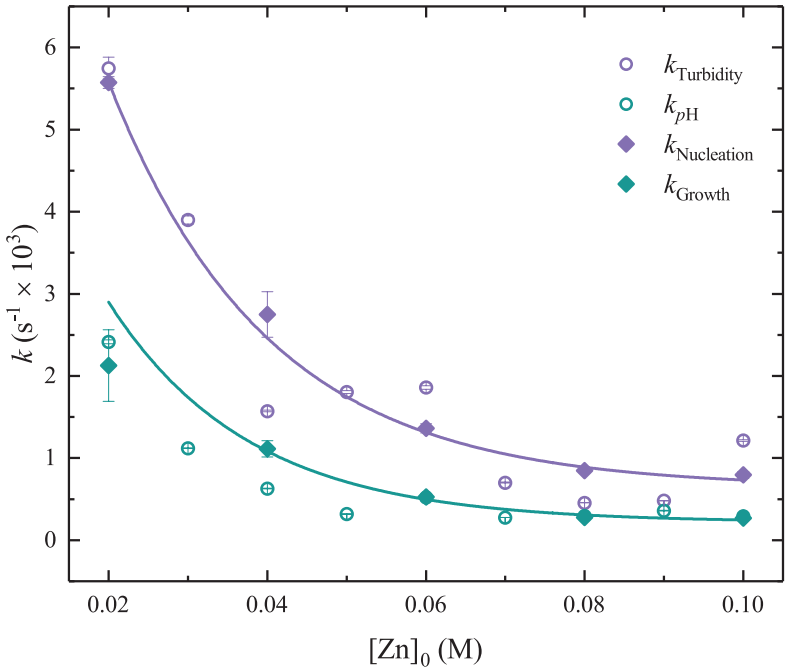
Case study 2

ZIF-8 formation



ZIF-8
Zn(2-methylimidazolate)$_2$






Mike Gaultois


Yue Wu

H. H.-M. Yeung, A. F. Sapnik, F. Massingberd-Mundy, M. W. Gaultois, Y. Wu, D. X. Fraser, S. Henke, R. Pallach, N. Heidenreich, O. Magdysyuk, N. T. Vo, A. L. Goodwin
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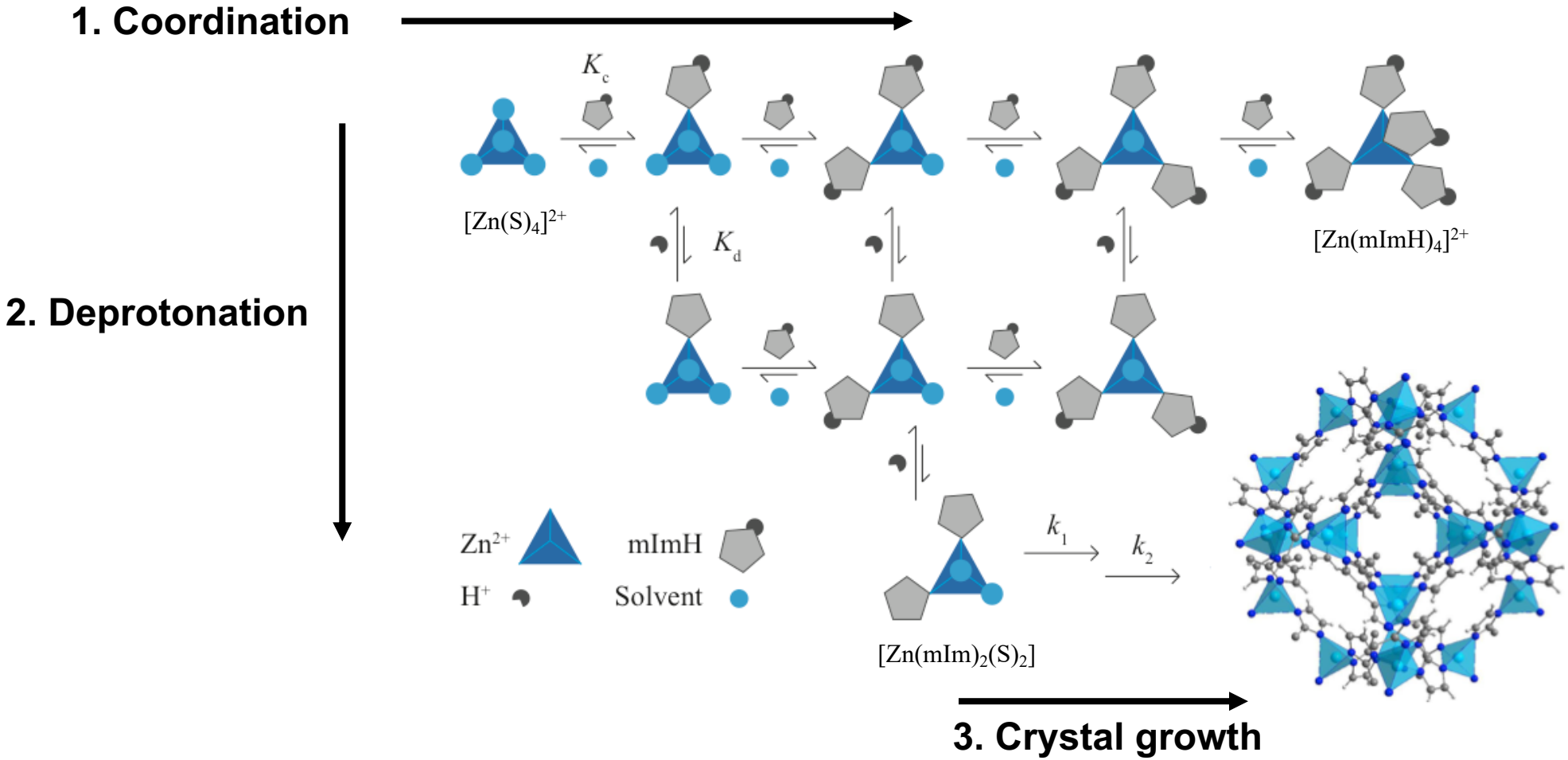
Pre-nucleation equilibria



H. H.-M. Yeung, A. F. Sapnik, F. Massingberd-Mundy, M. W. Gaultois, Y. Wu, D. X. Fraser, S. Henke, R. Pallach, N. Heidenreich, O. Magdysyuk, N. T. Vo, A. L. Goodwin
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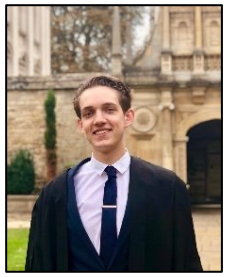
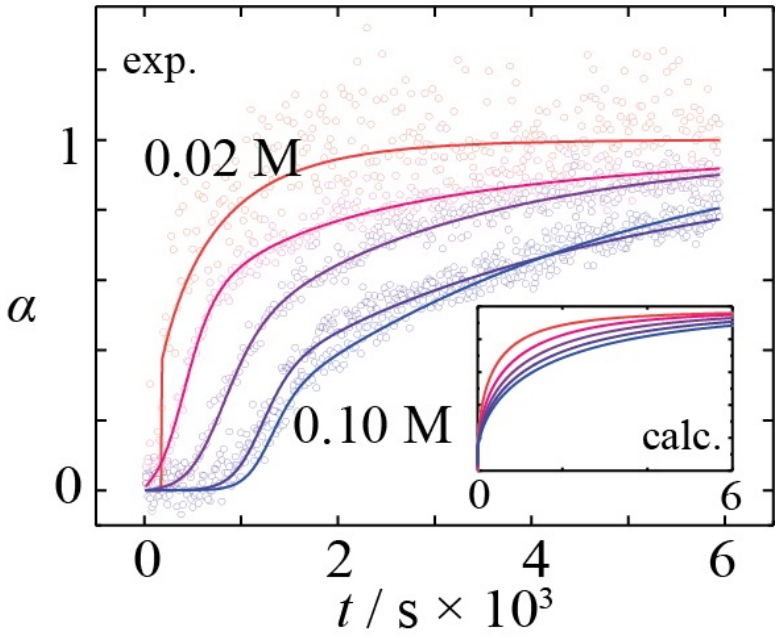
Model vs. experiment

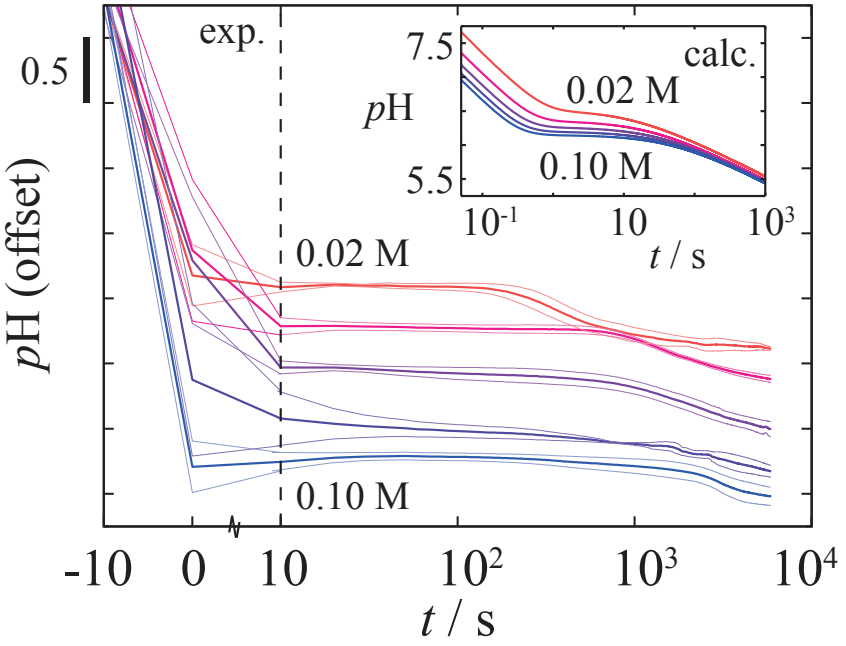
Felicity Massingberd-Mundy



Adam Sapnik



***In-situ* X-ray diffraction**

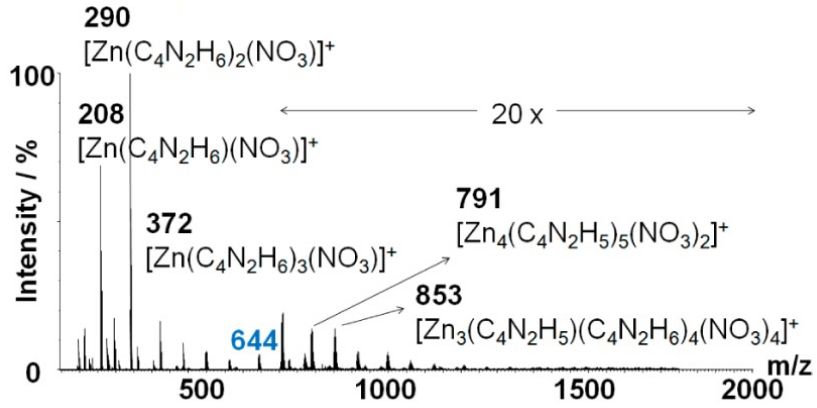


***In-situ* pH monitoring**

COPASI

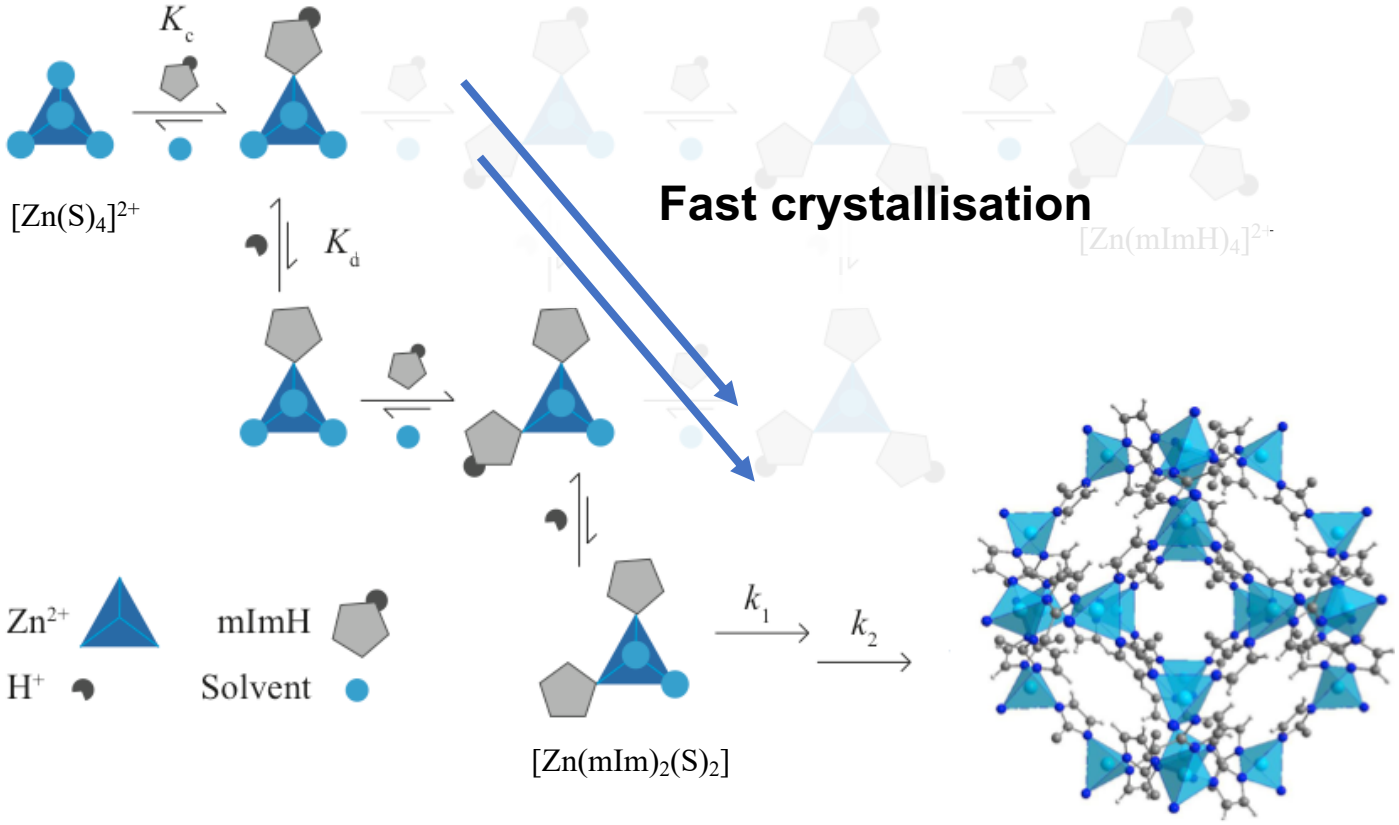
[Copasi programme] S. Hoops, *et al.*, *Bioinformatics* **2006**, *22,* 3067–3074.

Low concentration / high pH



Mass spectrometry

I. H. Lim, F. Schüth *et al.*, *Chem. Mater.* **2015**



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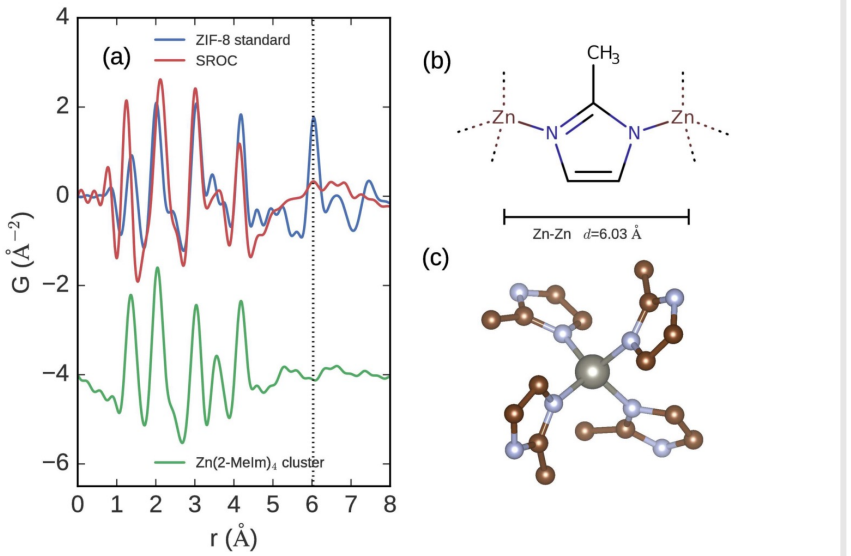
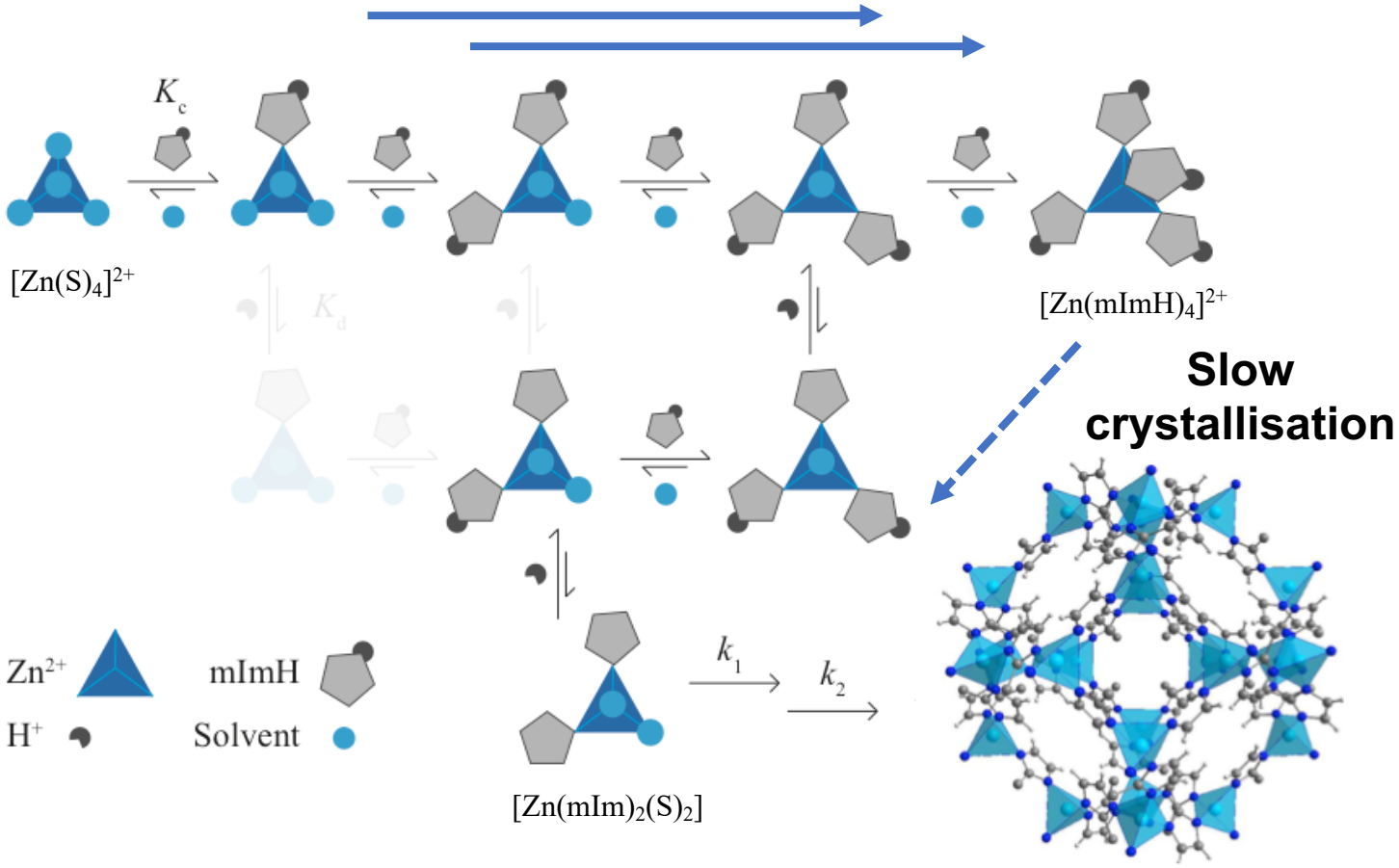
High concentration / low pH



Total scattering
M. Terban, S. J. L. Billinge *et al.*, *Nanoscale.* **2018**

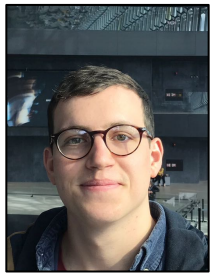


H. H.-M. Yeung, A. F. Sapnik, F. Massingberd-Mundy, M. W. Gaultois, Y. Wu, D. X. Fraser, S. Henke, R. Pallach, N. Heidenreich, O. Magdysyuk, N. T. Vo, A. L. Goodwin
Angewandte Chemie, International Edition **2019**, *58*, 566-571

Case study 3

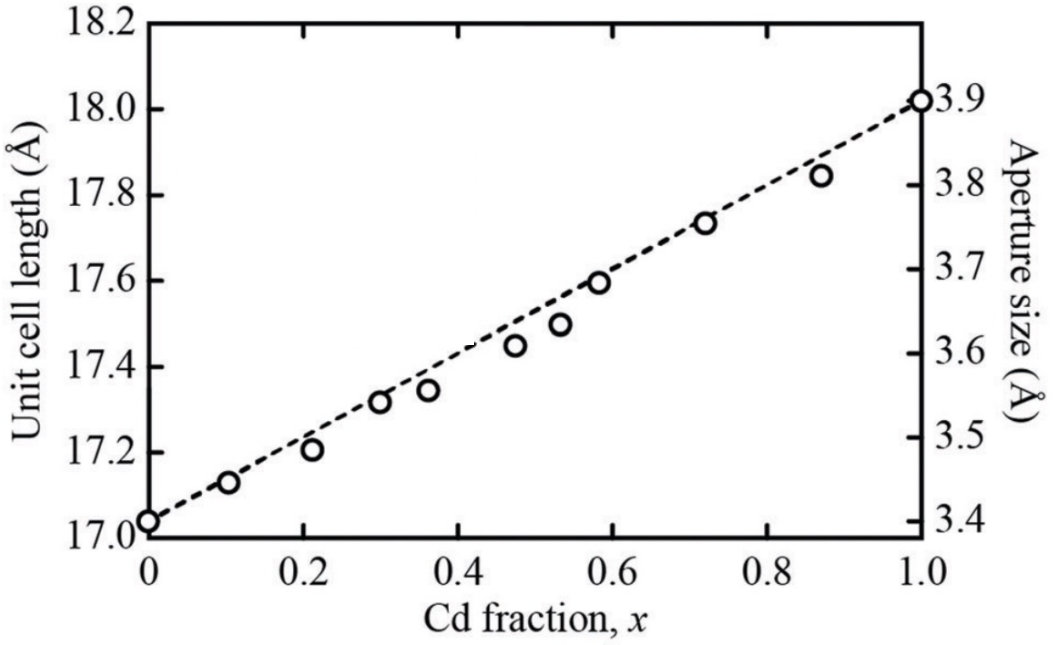
Mixed-component Zn/Cd-ZIF-8

Adam Sapnik

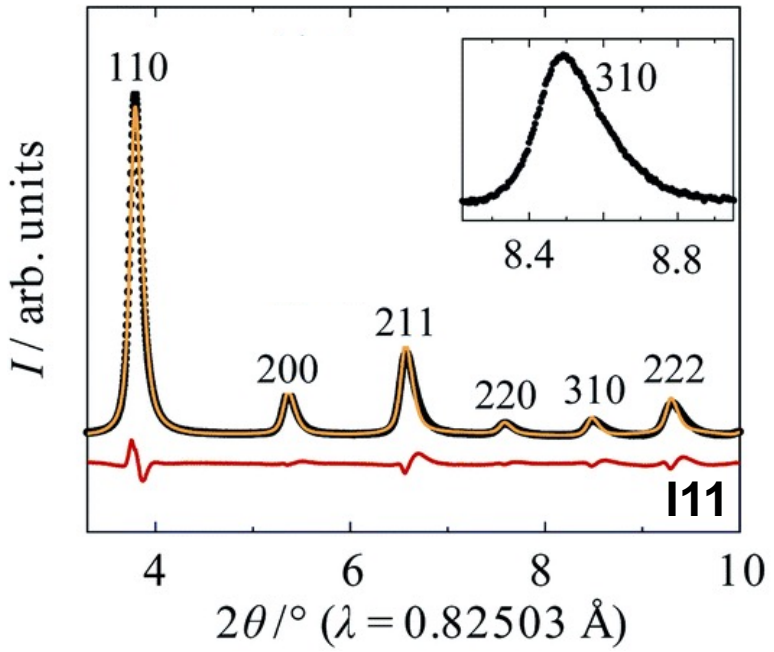


Kieran Orr

		[10.80, 10.83]	
		13 Al aluminium 26.98	
11	12		
29 Cu copper 63.55	30 Zn zinc 65.38(2)	31 Ga gallium 69.72	
47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	
79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium [204.3, 204.4]	
111	112		



Thermodynamic conditions[1]



Kinetic conditions[2]

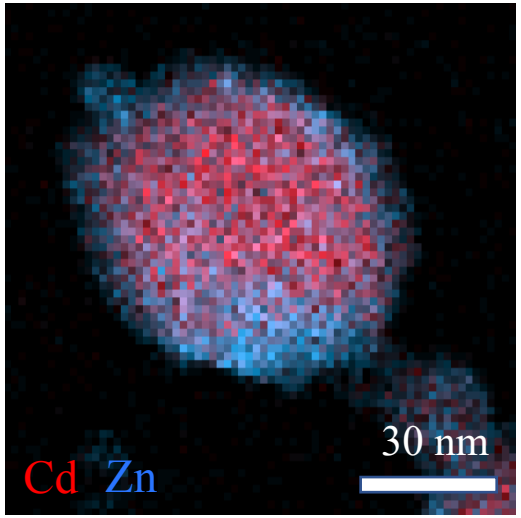
[1] A. F. Sapnik, H. H.-M. Yeung, A. L. Goodwin, *et al.*, *Chem. Commun.* **2018**, *54*, 9651–9654.
[2] K. W. P. Orr, S. M. Collins, A. L. Goodwin, H. H.-M. Yeung *et al.*, *Chemical Science* **2021**, *12*, 4494–4502.

UNIVERSITY OF OXFORD

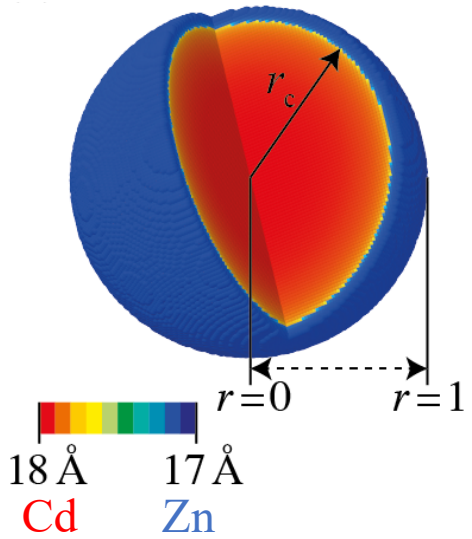
Core–shell nanoparticles

Sean Collins

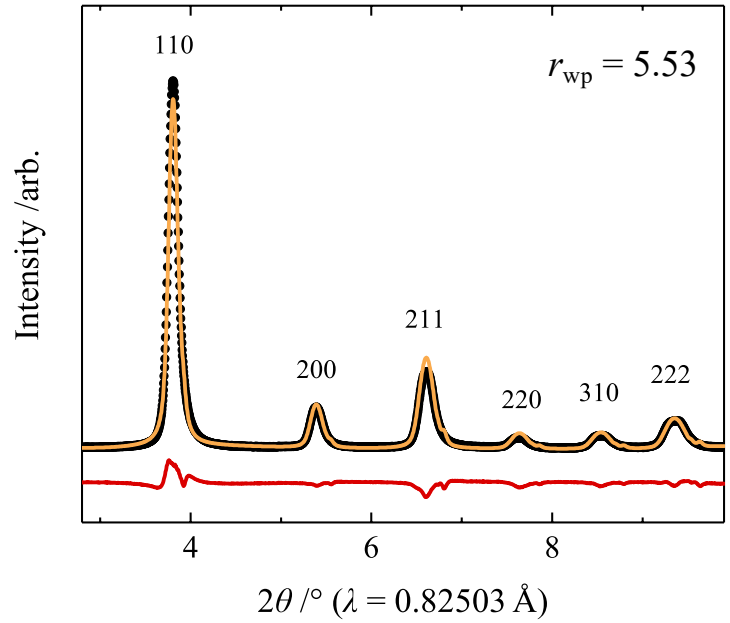
Andrew Goodwin



STEM–EDS



$$a(r) = a_c + \sigma \frac{|r_c - r|^{\nu+1}}{r_c - r}$$



a_c Lattice parameter at interface | σ Range of lattice parameters | r_c Nominal interface radius | ν Diffuseness

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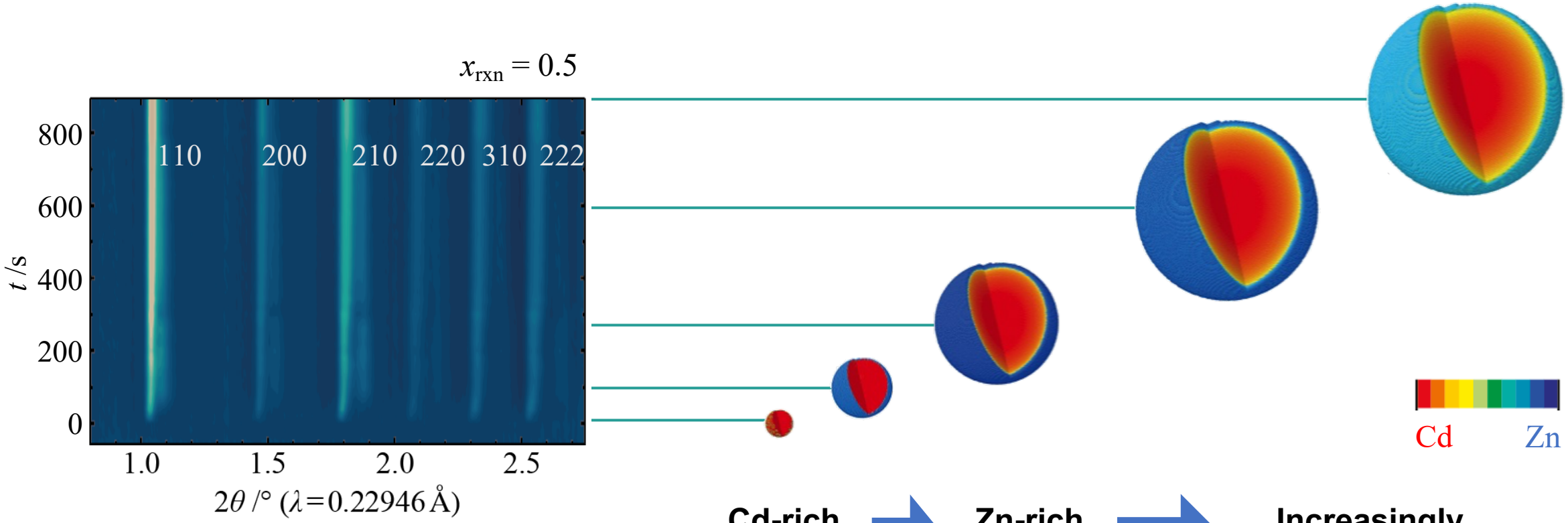
Chemical Science **2021**, *12*, 4494–4502.

Formation mechanism

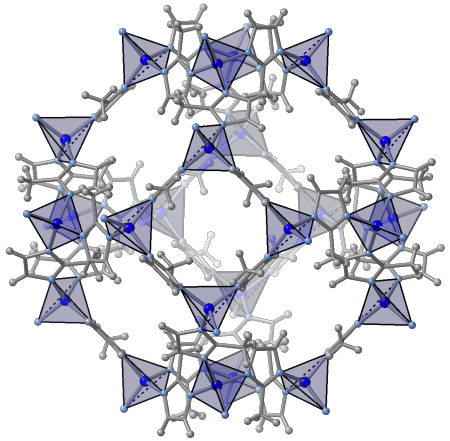


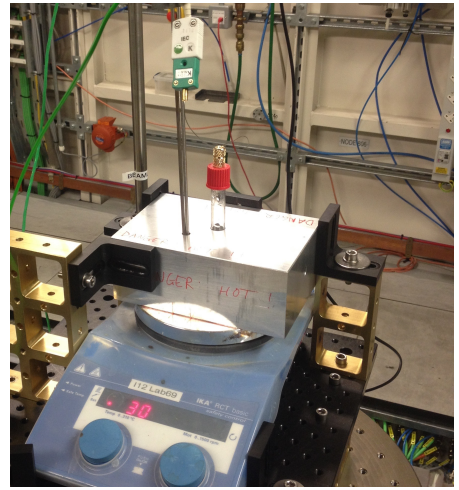
***In situ* X-ray diffraction**

Cd-rich nuclei → **Zn-rich shell** → **Increasingly diffuse interface**

K. W. P. Orr, S. M. Collins, E. M. Reynolds, F. Nightingale, H. Boström, S. J. Cassidy, D. Dawson, S. E. Ashbrook, O. V. Magdysyuk, P. A. Midgley, A. L. Goodwin, H. H.-M. Yeung
Chemical Science **2021**, *12*, 4494–4502.

Summary

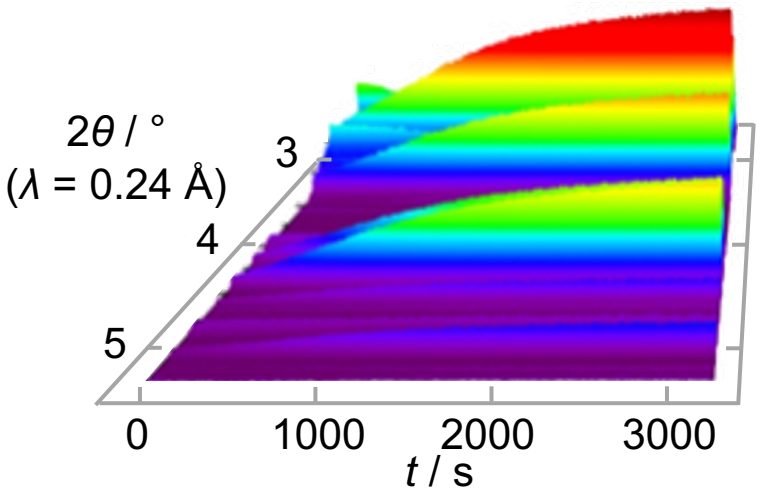




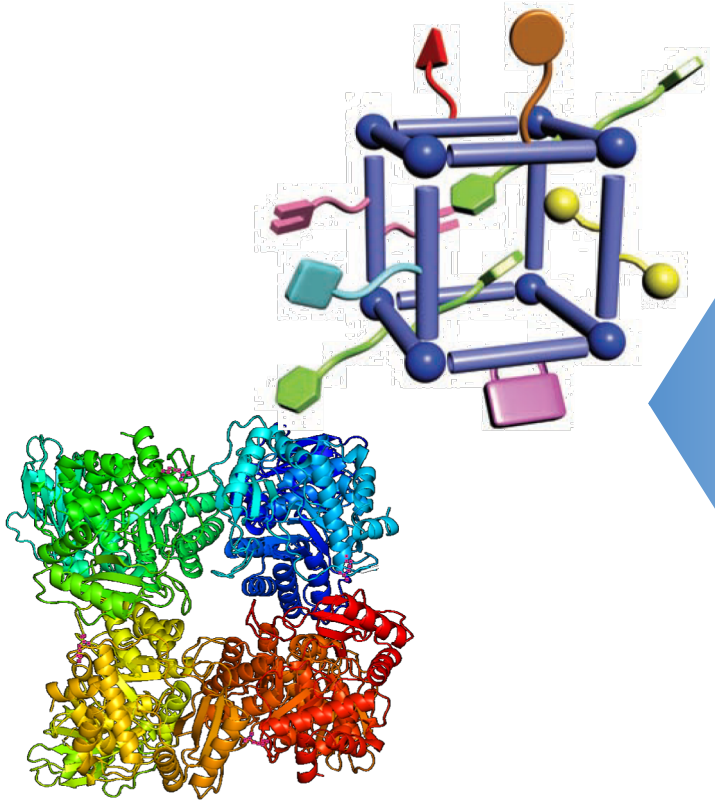
1. **Framework materials**
   - Topology + chemistry

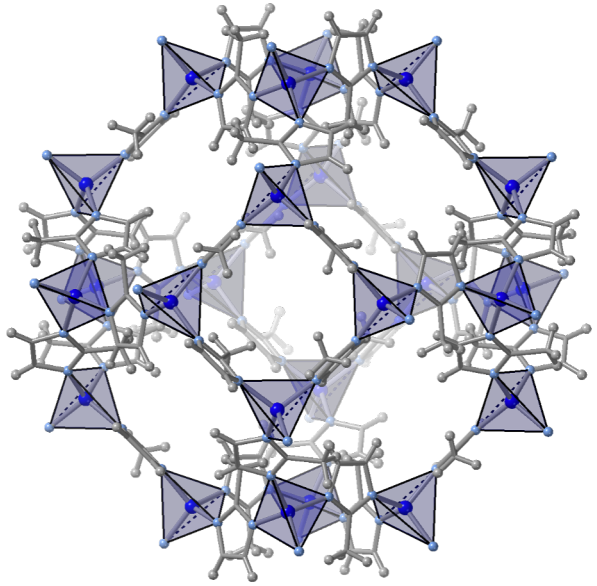
2. **Formation studies**
   - Capabilities of *in-situ* experiments
   - Extracting quantitative information

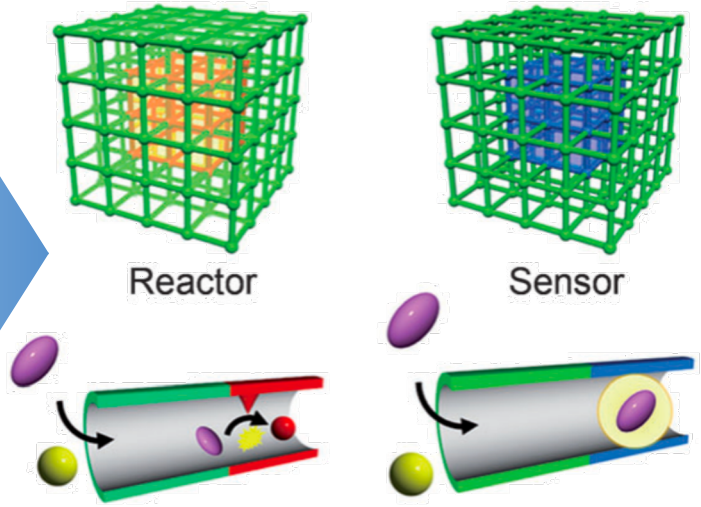
3. **Case studies**
   - Lithium tartrate polymorphism
   - ZIF-8 non-linear crystallisation
   - Zn/Cd-ZIF-8 nanoparticles



The future is more than average







Mixed components[1,2]

Bulk structure

Phase separation[3]

[1] H. Deng, O. Yaghi *et al.*, *Science* **2010**, *327*, 846–850.
[2] Adapted from "SpinachRuBisCO.png" under a CC BY-SA 4.0 licence, Wikipedia.org user Ericlin1337.
[3] K. Hirai, S. Kitagawa *et al.*, *Angew. Chem.* **2011**, *50*, 8057-8061.

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