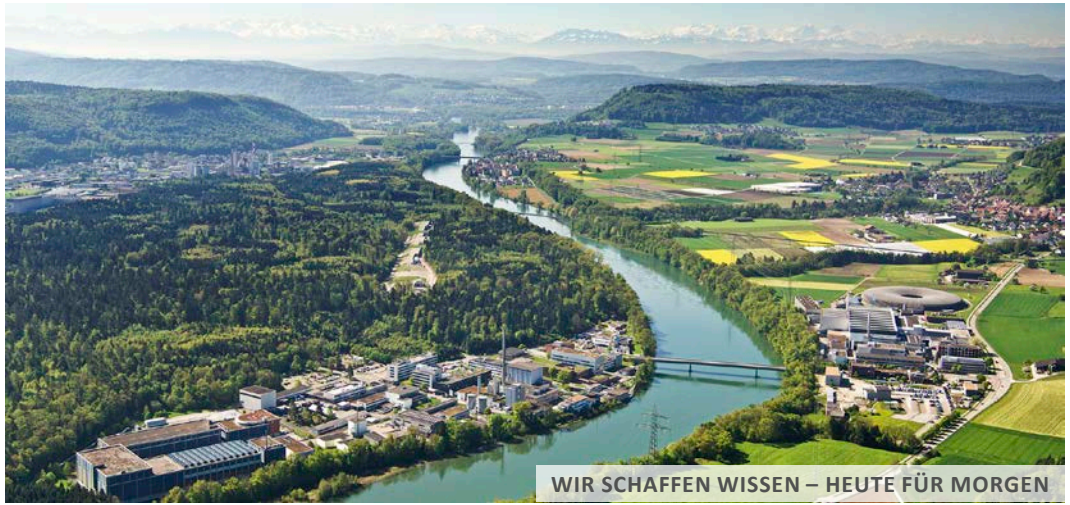
PAUL SCHERRER INSTITUT

PSI



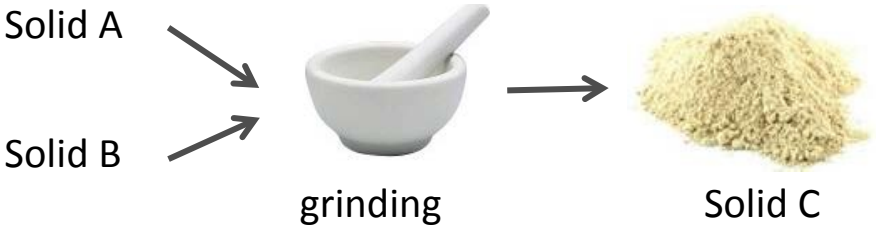
Manuel Wilke:: PSI-Fellow :: Paul Scherrer Institut

Formation of hybrid organic-inorganic guanidinium lead(II) iodides from mechanochemical reactions

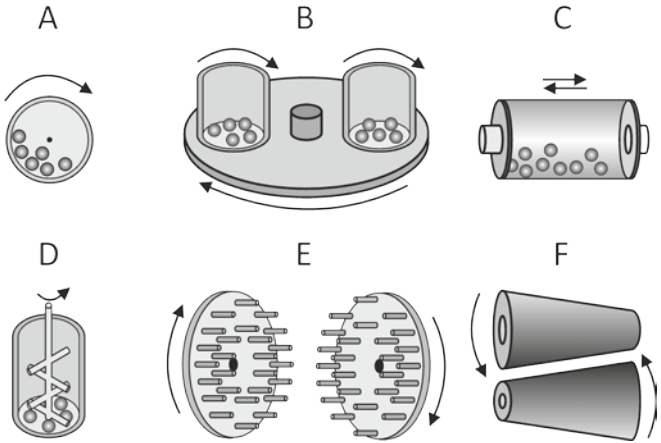
Empa Postdocs-II & PSI-FELLOW II-3i RETREAT 2018

Mechanochemical Syntheses

Mechanochemistry: “a chemical reaction that is induced by the direct absorption of mechanical energy” (IUPAC)



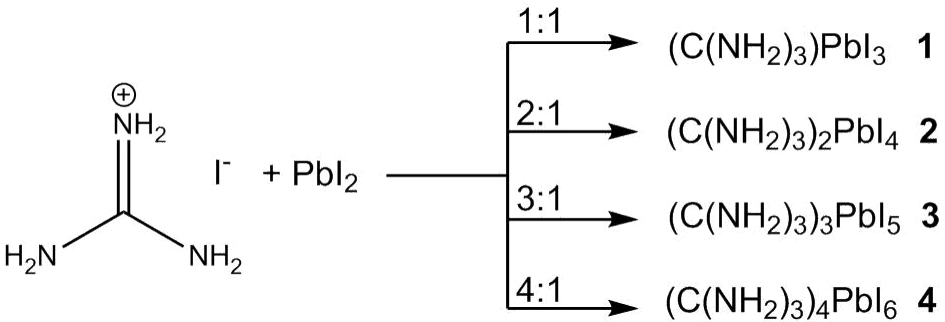
Mechanical activation creates defects, but the real mechanisms are still unknown and several theories exist



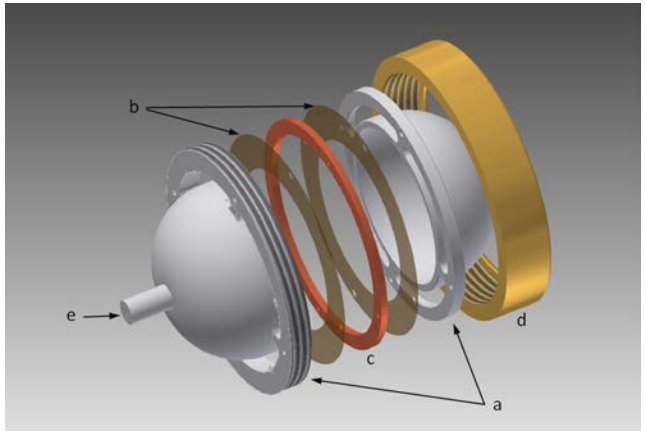
Types of mills for high-energy milling: A: ball mill, B: planetary mill, C: vibration mill, D: attritor (stirring ball mill), E: pin mill, F: rolling mill.

P. Balaz, *Chem. Soc. Rev.* **2013**, *42,* 7571-7637.

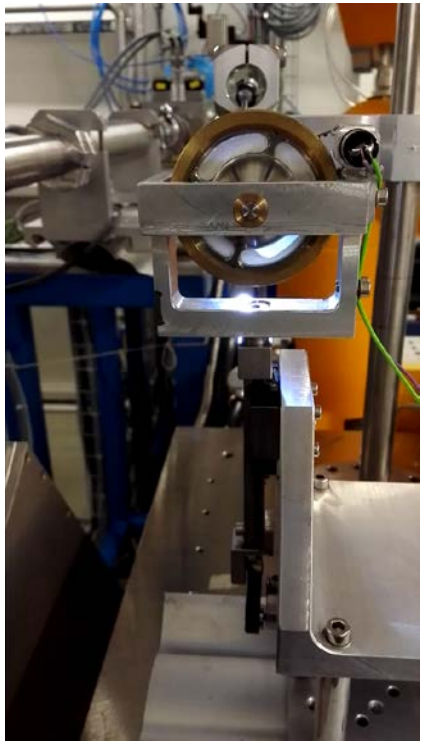
Labsyntheses



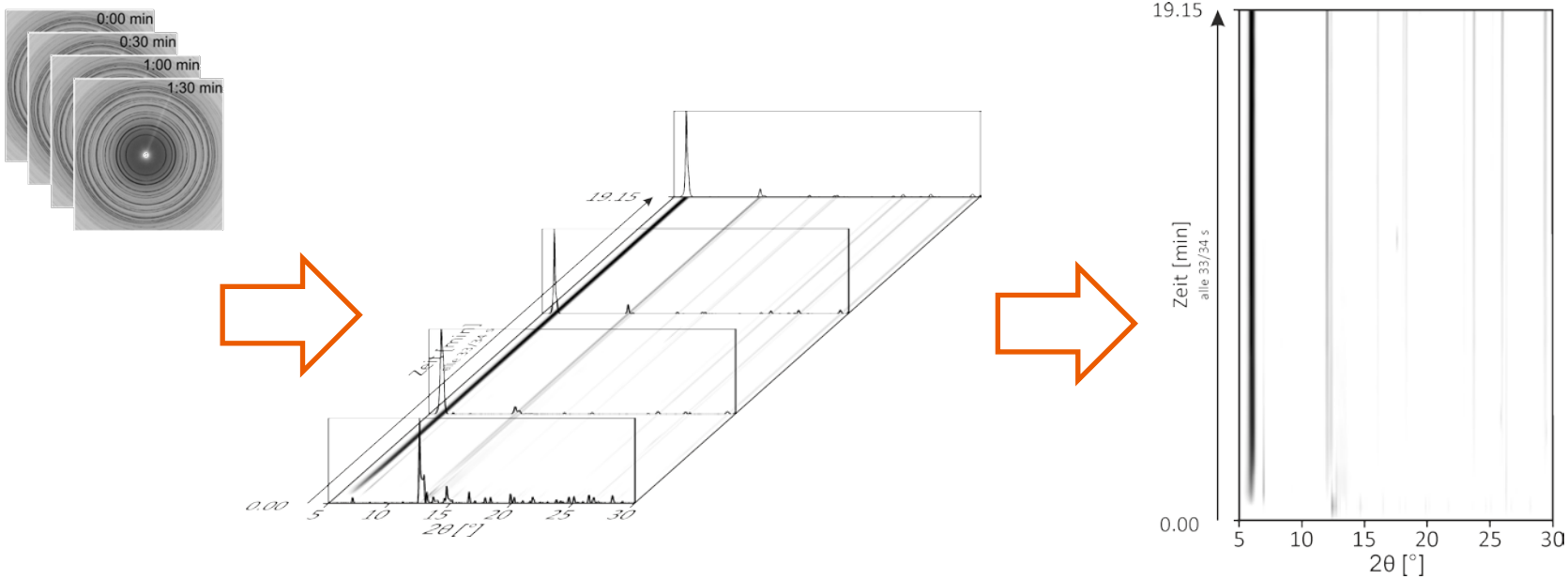
In situ setup



V. Ban *et al. Anal. Chem*. **2017**, *89*, 13176-13181.

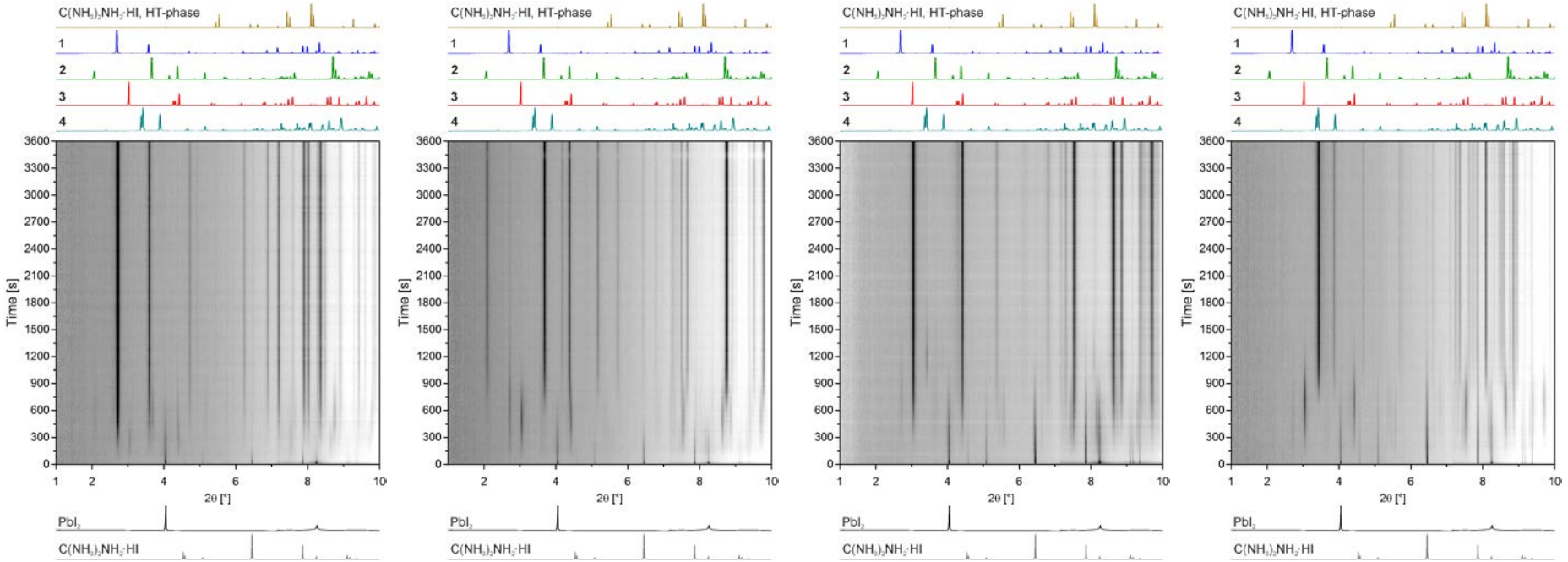


In situ setup



In situ investigations

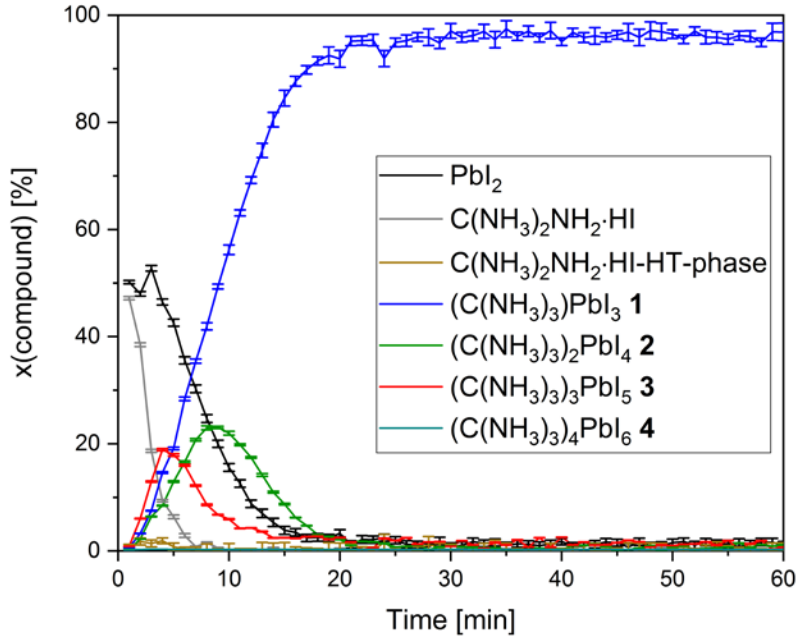
$(C(NH_3)_3)PbI_3$ **1**	$(C(NH_3)_3)_2PbI_4$ **2**	$(C(NH_3)_3)_3PbI_5$ **3**	$(C(NH_3)_3)_4PbI_6$ **4**



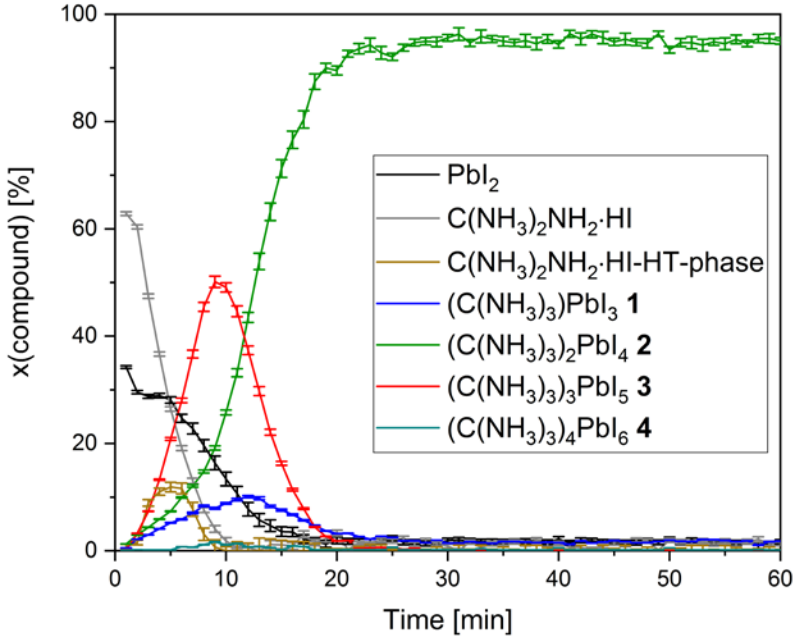
M. Wilke, N. Casati, *Chem. - Eur. J.* **2018**, *accepted*

In situ investigations

$(C(NH_3)_3)PbI_3$ **1**



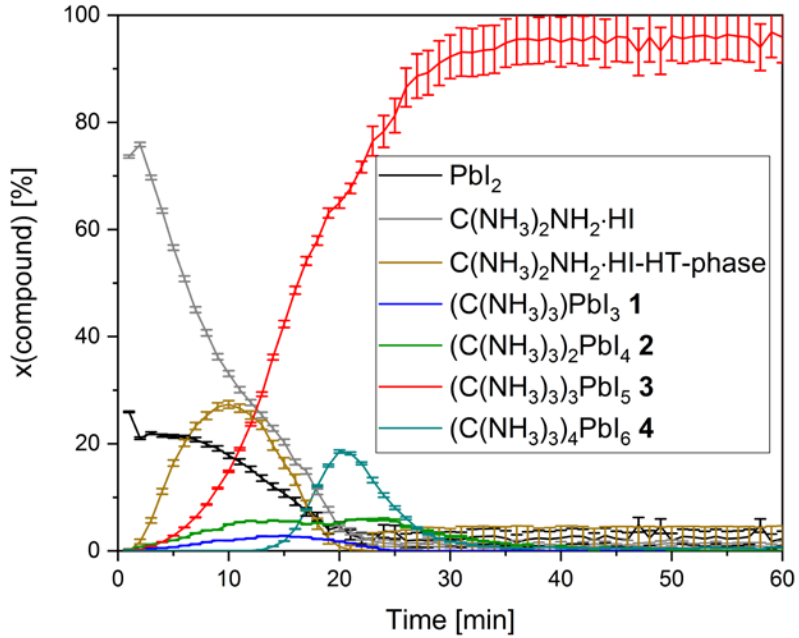
$(C(NH_3)_3)_2PbI_4$ **2**



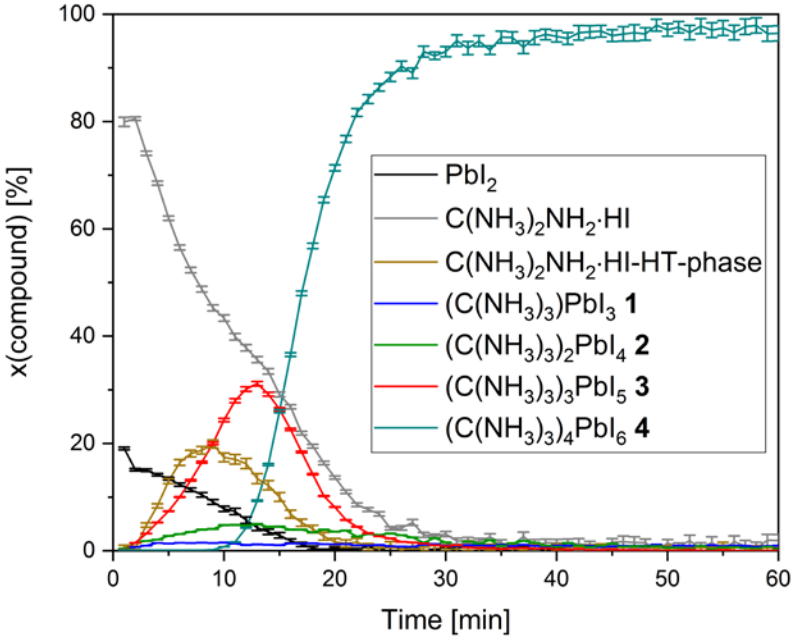
M. Wilke, N. Casati, *Chem. - Eur. J.* **2018**, *accepted*

In situ investigations

$(C(NH_3)_3)_3PbI_5$ **3**



$(C(NH_3)_3)_4PbI_6$ **4**



M. Wilke, N. Casati, *Chem. - Eur. J.* **2018**, *accepted*

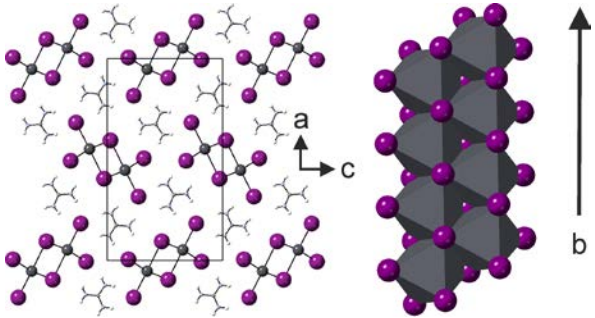
In situ investigations

Compound	Nucleation	Growth	Shrinking
1	Fast	Slow	Slow
2	Medium	Slow	Slow
3	Fast	Fast	Fast
4	Very slow	Fast	Fast

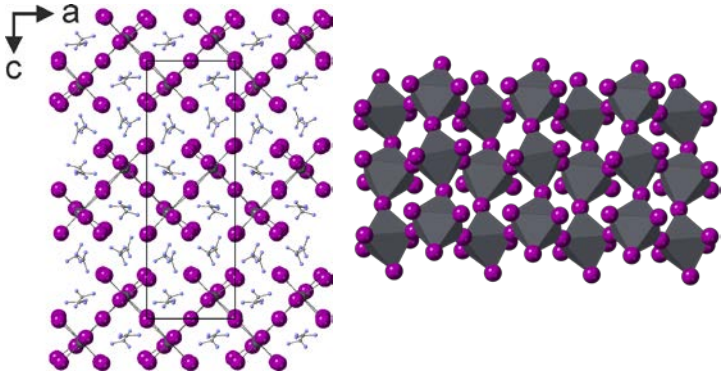
- Are nucleation and growth related to crystal or framework structure?
- Similar speed for growth and shrinking → dependent on framework stability
- H-bonds between amine and I- getting stronger from compound 1-4
  → growth speed follows that order

In situ investigations

$(C(NH_3)_3)PbI_3$ **1**



$(C(NH_3)_3)_2PbI_4$ **2**



M. Daub *et al. Eur. J. Inorg. Chem*. **2017**, *2017*, 1120-1126.

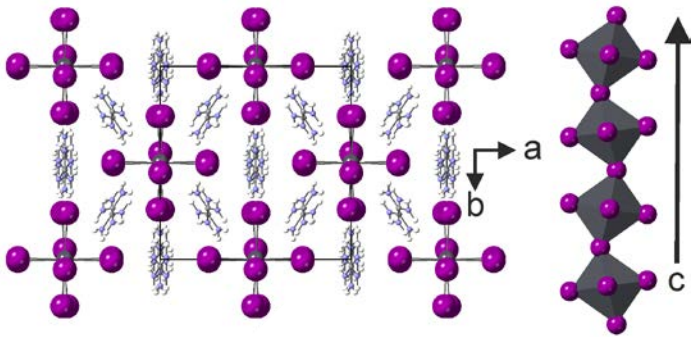
- Fast to medium nucleation speed but slow growth
  → dense ribbon- or 2D structure, requires more connections

M. Wilke, N. Casati, *Chem. - Eur. J.* **2018**, *accepted*

In situ investigations

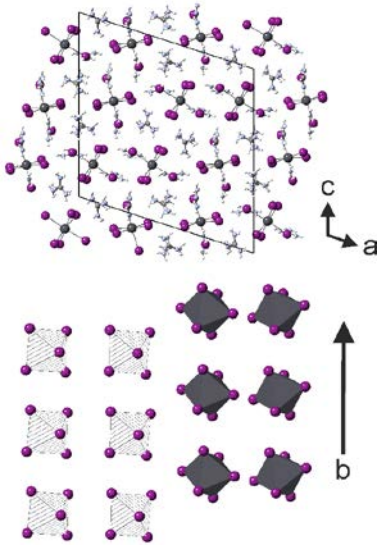
$(C(NH_3)_3)_3PbI_5$ **3**

- Fast nucleation and fast growth
  → simple 1D chain structure, easy to build



$(C(NH_3)_3)_4PbI_6$ **4**

- Very slow nucleation speed but fast growth
  → isolated $[PbI_6]^{4-}$ octahedra
- →critical amount needed for nucleation
- If reached, growth is just an arrangement of the single units



M. Wilke, N. Casati, *Chem. - Eur. J.* **2018**, *accepted*

Summary

- Mechanochemistry suitable for synthesizing hybrid lead(II)-iodides
- Final product by stoichiometric control
- Reaction pathways guided by the complexity of the inorganic moiety and the strength of the present H-bonds

- Thanks to:
  - Nicola Casati (group leader)
  - Tomasz Poreba (PhD)

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