



# Building crystalline ladders with a ditopic ligand

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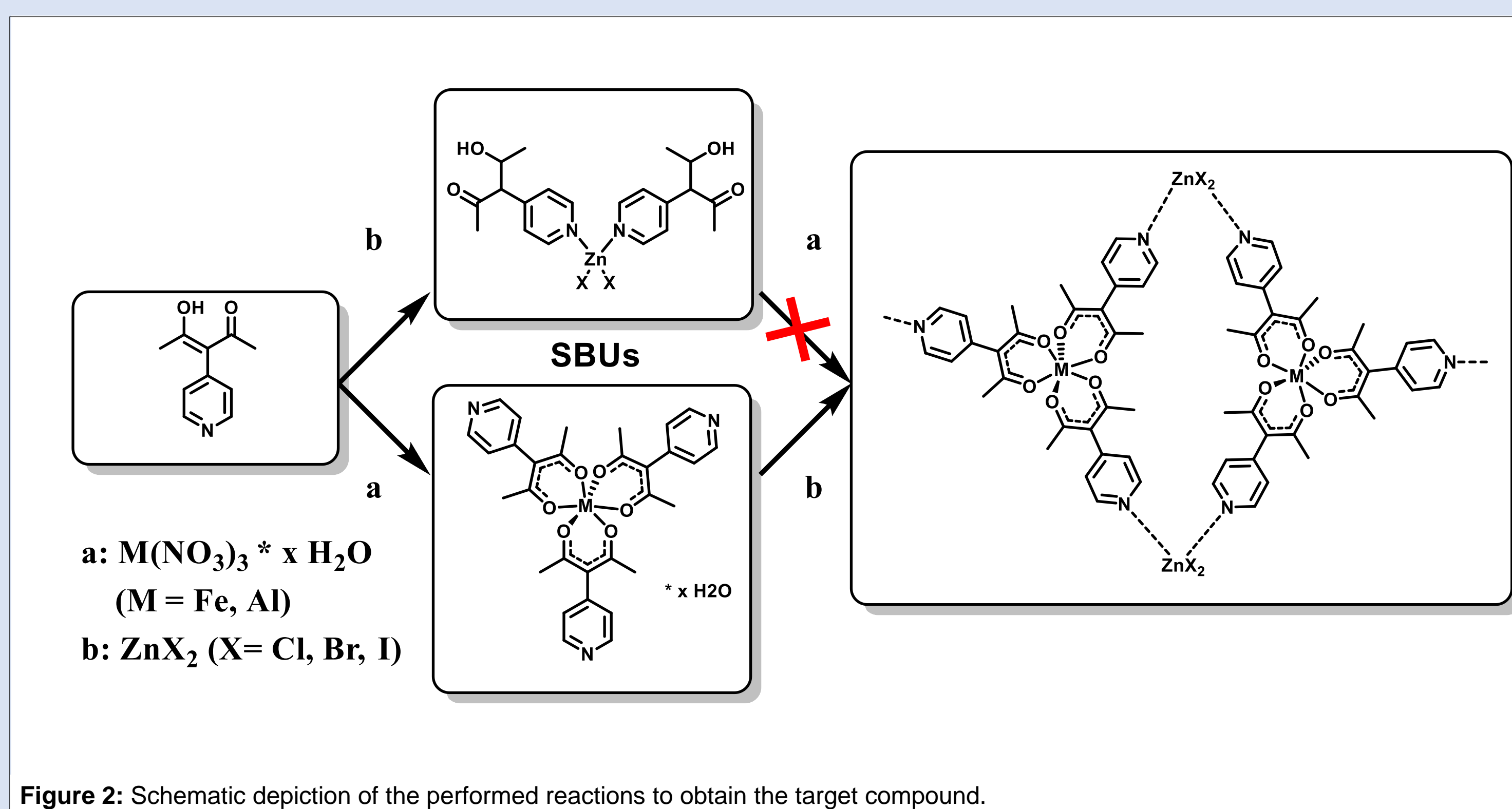
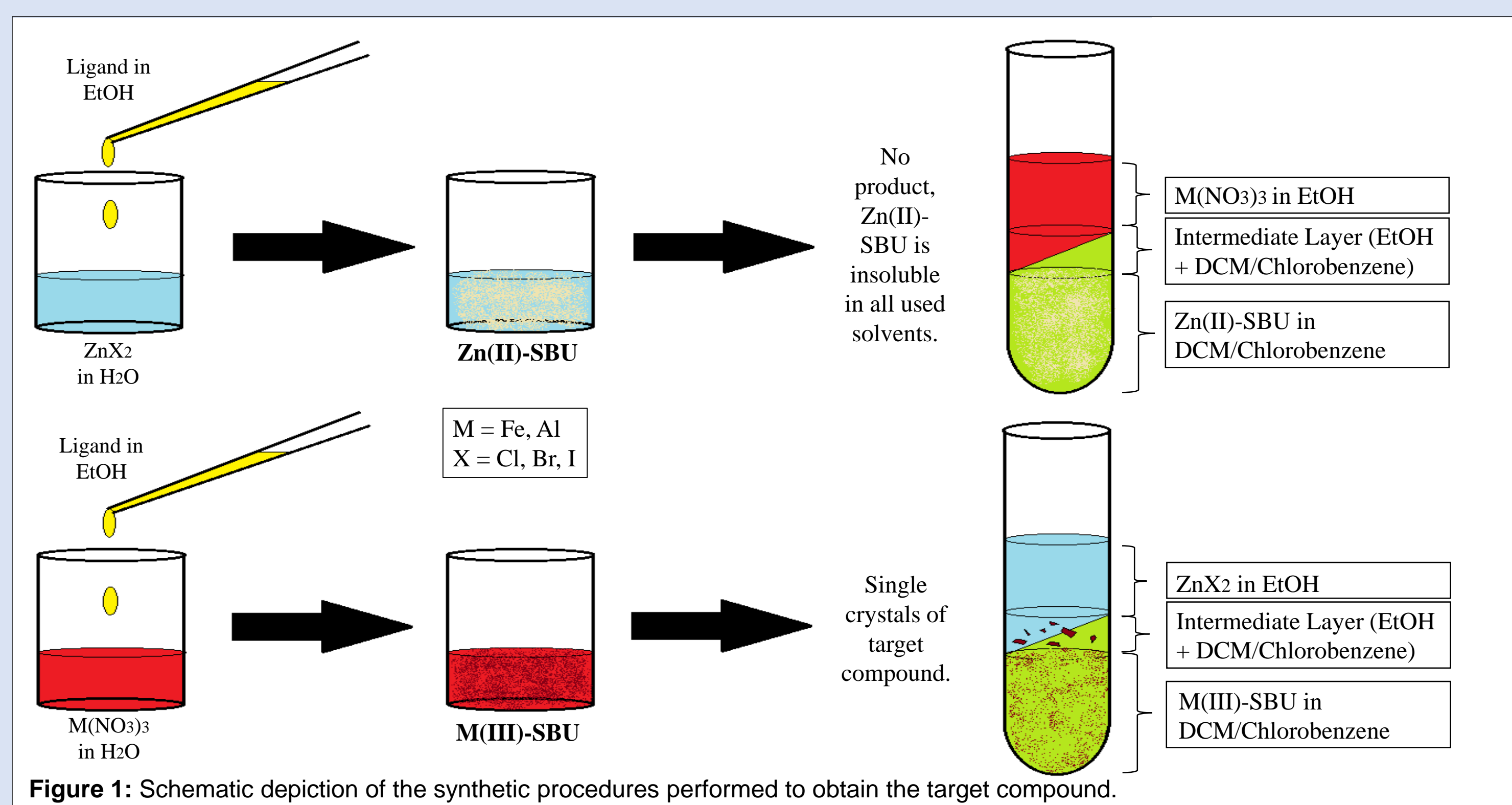
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## Introduction

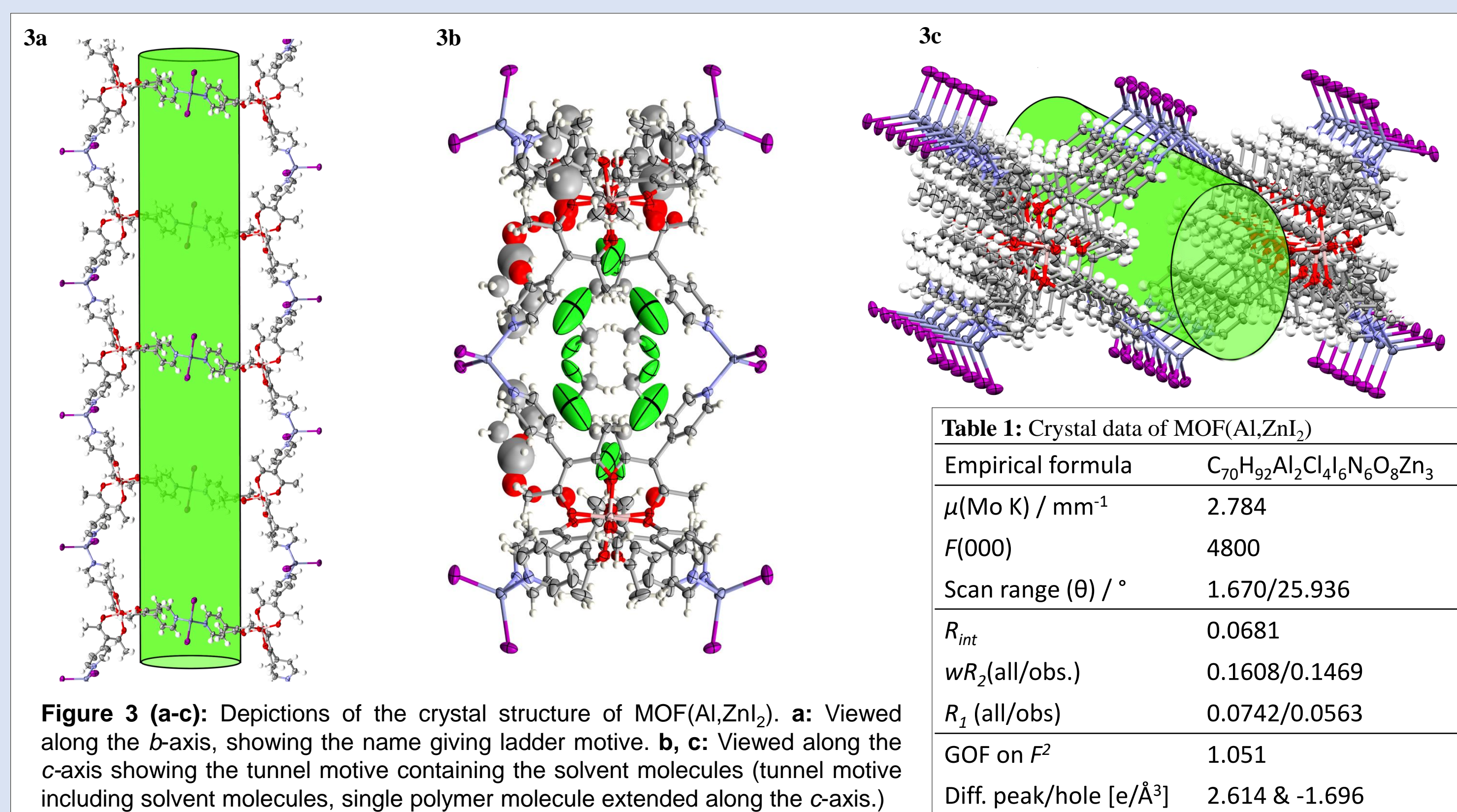
Crystal engineering, the prediction and synthesis of crystal structures by careful selection of reactants, solvents and conditions, has grown in popularity over the last decades. Though many crystal structures obtained through crystal engineering have been published in the last years, a precise prediction of the self assembly processes is still difficult, if not impossible. The self assembly can be controlled through the use of secondary building units (SBUs), coordination compounds that can be analyzed as an intermediate of the reaction, and through a good understanding of the properties of the used organic linker molecules, the ligands. One example of crystal engineering is presented here. The ditopic ligand 3-(4-pyridyl)-acetylacetone (HacacPy) was used to create two SBUs, for which further coordination was then attempted. 3-(4-pyridyl)-acetylacetone features two coordination sites with distinct properties that allow a targeted coordination to certain metal cations. The soft pyridyl *N* can coordinate to equally soft metal cations, in this case Zn(II), while the hard, chelating oxygen atoms of the acetylacetone can be coordinated to harder metal cations like Al(III) or Fe(III), after deprotonation.

## Synthesis



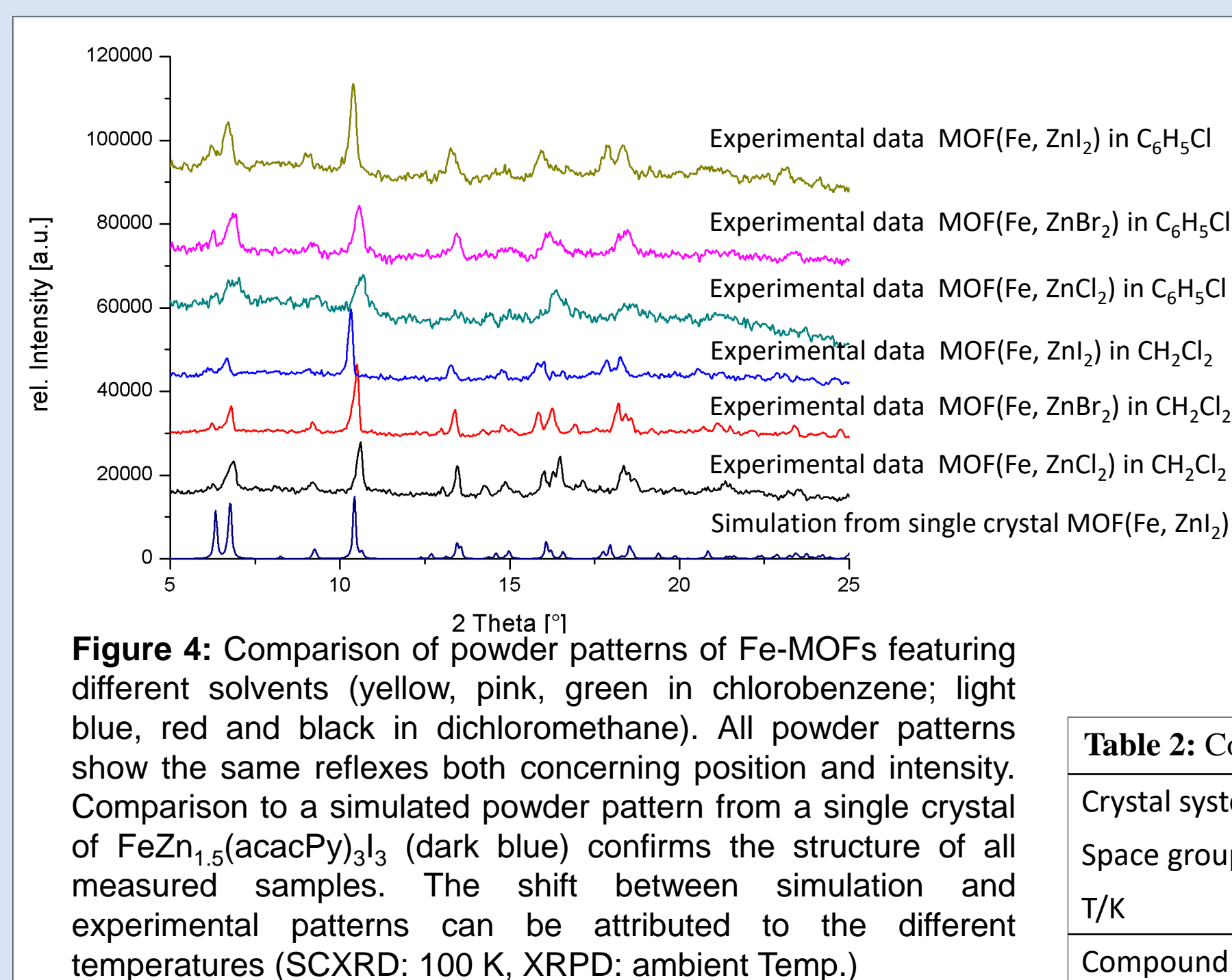
In principle, the framework may be synthesized via two routes, however product can only be obtained for one method. The chelating coordination of the oxygen site of HacacPy requires a prior deprotonation. This is usually performed by adding an adequate amount of a mild base (e.g. NaHCO<sub>3</sub>) to the ligand solution before coordination.

## Crystal Structures



The crystal structure was obtained on a Bruker APEX Diffractometer and solved using SHELX. Refinement of the structure model was hampered by the large amount of solvent molecules inside the framework, and remaining electron density around the heavy atoms, especially iodine. 25 restraints were introduced to refine most of the solvent molecules anisotropically while attaining a sensible structural model.

## Isomorphism



All found structures exhibit isomorphism, meaning that all compounds crystallize in the same space group with closely related coordinates. Powder diffraction for all six compounds confirms similar intensity patterns and unit cell parameters

**Table 2:** Comparison of unit cells of all obtained compounds.

Crystal system	Monoclinic		
Space group (no.)	I2/a (15)		
T/K	100(2)		
Compound	MOF(Al,ZnCl <sub>2</sub> )	MOF(Al,ZnBr <sub>2</sub> )	MOF(Al,ZnI <sub>2</sub> )
a / Å	26.626(2)	26.802(2)	27.252(2)
b / Å	13.7515(7)	13.8103(3)	13.8519(8)
c / Å	27.2123(15)	27.3069(16)	27.7528(16)
$\beta$ / °	111.2460(10)	110.1330(10)	109.5680(10)
V / Å <sup>3</sup>	9286.7(10)	9490(12)	9871.4(12)
Compound	MOF(Fe,ZnCl <sub>2</sub> )	MOF(Fe,ZnBr <sub>2</sub> )	MOF(Fe,ZnI <sub>2</sub> )
a / Å	26.345(5)	26.540(4)	27.0136(18)
b / Å	13.6113(17)	13.694(2)	13.87460(10)
c / Å	27.028(4)	27.236(6)	27.503(3)
$\beta$ / °	110.855(2)	110.095(2)	109.0510(10)
V / Å <sup>3</sup>	9057(2)	9296(3)	9743.8(12)

A small increase in size can be observed for the different structures in correlation to the size of the used metal anions as well as the used halides. The isomorphism is also retained when switching the solvents used during the crystallization from dichloromethane to chlorobenzene.

## Conclusion

Through crystal engineering, we were able to create a set of previously unknown coordination compounds. The six obtained compounds are all isomorphous, crystallizing in a one dimensional „ladder“ conformation. The isomorphism of the compounds was affirmed both by single crystal X-ray diffraction as well as powder X-ray diffraction. The crystallization experiments were performed using two different solvents, DCM and chlorobenzene. Since the powder patterns of all compounds are identical, regardless of the used solvents, we can assume that the incorporated solvents do not affect the coordination polymer, and can be exchanged without destroying the structure. While we only investigated the crystallization from two different solvents, it seems reasonable that other solvents can be contained in the same crystal structure. While two principle synthesis routes are reasonable and were attempted, only one of the routes yielded the product, showing once more the importance of clever crystal engineering.

## Acknowledgement

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