

Lattice modification and morphological control of halide substituted *yqt*-type zeolitic imidazolate frameworks Zn_3mim_5X , with $X = Br, Cl, F$ or OH

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Zeolitic Imidazolate Frameworks (ZIFs) are a large subgroup of metal-organic frameworks, which has been studied for almost 90 years. In this study, we describe the synthesis of ZIF phases showing an *yqt* type framework by the reaction of methylimidazole (Hmim) with a zinc salt in aqueous solution. The use of different zinc salts like acetates, nitrates, chlorides, fluorides, bromides, iodides and sulfates does not only lead to different morphologies (Fig. 1, a, b) but also to different products: $Zn_3mim_5XH_2O \cdot n H_2O$ with $x = Br, Cl$ and α - Zn_3mim_5X with $x = F, OH$ [1, 2]. By thermal dehydration of the hydrated ZIF phase, a series of isostructural compounds, α - Zn_3mim_5X with $x = Br, Cl, F$ or OH was obtained. The crystal structures were solved *ab initio* from X-ray powder diffraction (XRPD) data and the products studied by vibrational and solid state NMR spectroscopy. In all structures, zinc exhibits a tetrahedral coordination (Fig. 1, c, d) and forms an *yqt* net. Inorganic anions are incorporated into this net as Zn-X-Zn bridges (Fig. 1, e, red bonds) and show a major impact on the reversible de- and rehydration behavior, as well as on the thermal expansion. The latter property is mainly governed by the bending of the Zn-X-Zn bridge. Within the series of isostructural, anhydrous *yqt*-type ZIF compounds, only the chloride containing phase, which shows strongest anisotropic thermal expansion exhibits two polymorphs: α - and β - Zn_3mim_5Cl (Fig. 1, f), the α - form showing a bent and the β -form a linear Zn-X-Zn bridge. In conclusion, although the inorganic anion X is only a minor component in the sum formula of the investigated ZIF phases, it has a major impact on the properties, which opens up new perspectives for crystal engineering of these materials.

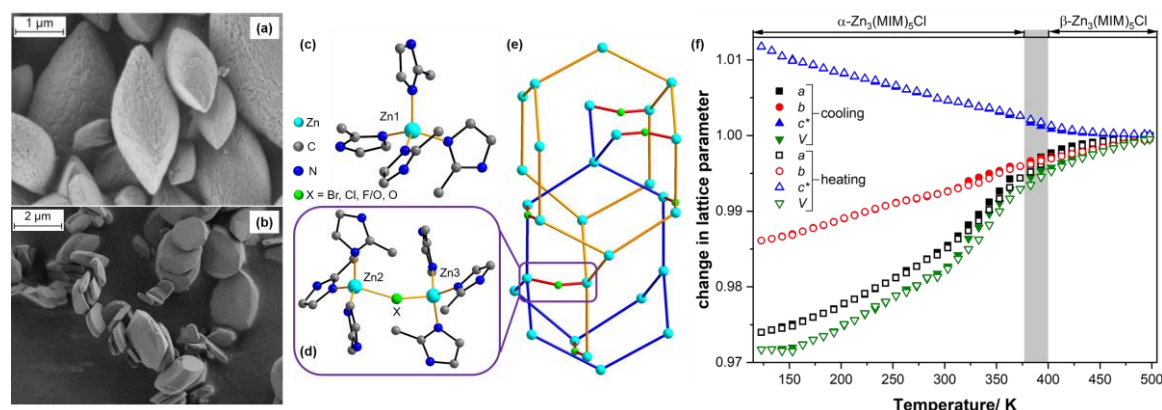


Fig 1. SEM images of (a) $Zn_3mim_5ClH_2O \cdot 0.74 H_2O$ and (b) $Zn_3mim_5(F_{0.33}[OH]_{0.67})$, (c), (d) Coordination spheres of the zinc cations in the crystal structures of α - Zn_3mim_5X compounds, (e) underlying connected tfa-c nets forming an *yqt1* net, (f) evolution of the lattice parameters during heating and cooling of Zn_3mim_5Cl

- [1] Glante S, Bette S, Gallo G, Dinnebier RE, Hartmann M. Crystal structure and de- and rehydration behavior of two new chloride-containing Zeolitic Imidazolate Frameworks. *Cryst. Growth & Design*, 19, 4844-4853 (2019)
- [2] Glante S, Wisser D, Hartmann M, Joos M, Dinnebier RE, Bette S. Lattice modification and morphological control of halide substituted *yqt*-type zeolitic imidazolate frameworks Zn_3mim_5X , with $X = F, Br, Cl$ or OH . *in preparation* (2022)