Fatty acid capped, metal oxo clusters as the smallest conceivable nanocrystal prototypes; from synthesis to application

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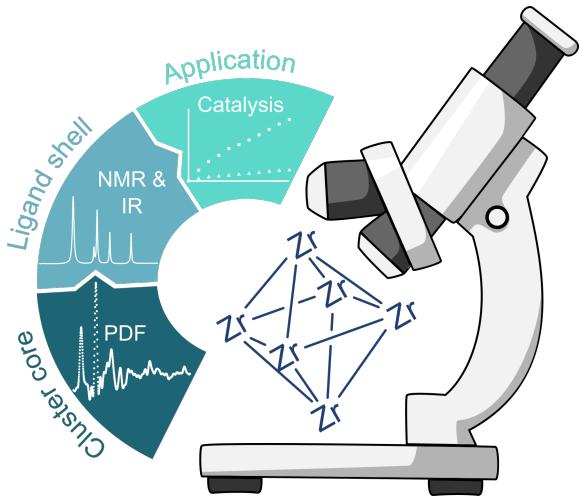
Group 4 metal oxo clusters M6O4(OH)4(RCOO)12 (M = Zr or Hf) are interesting materials with applications in 3D-printing, MOF's and catalysis.[1] We regard them as the smallest conceivable nanocrystals, since their inorganic core still resembles the crystalline oxide structure and it is capped with organic ligands, similar to colloidal nanocrystals. Despite their potential, only short and rigid ligand were explored limiting their solubility, but allowing for structure determination using single-crystal XRD.



Here we present the first comprehensive strategy on how to fully characterize zirconium oxo clusters, including both the inorganic core and the organic ligand shell.[2] We optimized the synthesis, achieving high yield and reproducibility, and extended the library of possible ligands to typical ligands used in the nanocrystal field. In order to obtain structural data, detailed Pair Distribution Function (PDF) analysis was used. The organic ligand shell is probed via NMR, TGA and IR. Our results were found to be applicable for hafnium oxo clusters as well. Finally, we show that these clusters as catalysts outperform nanocrystals 5-fold in esterification reactions. Additionally, they can be applied as liquid monomers/catalysts in the first ever covalent adaptable nanocomposites.

[1] Van den Eynden, D.; Pokratath, R.; De Roo, J., Chemical Reviews, **2022**.
[2] Van den Eynden, D.; Pokratath, R.; Mathew, J. P.; Goossens, E.; De Buysser, K.; De Roo, J., Chemical Science **2022**.