Institute of Nanotechnology (INT)
Karlsruhe Institute of Technology

Polyoxometalate-Based Functional Nanoscale Systems

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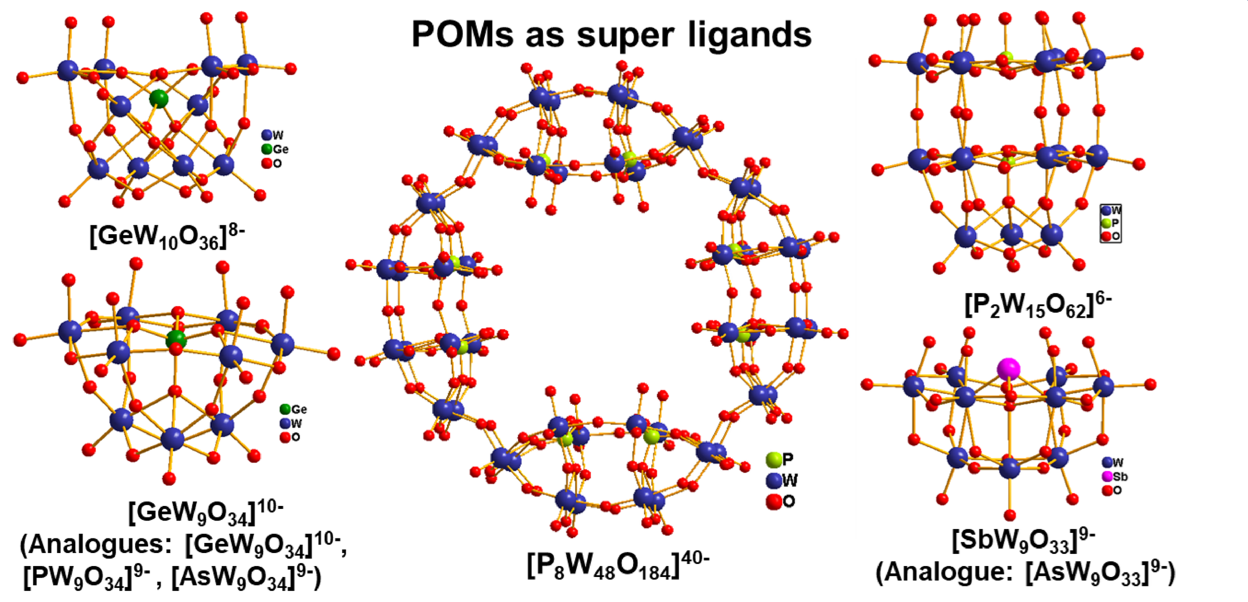
Introduction

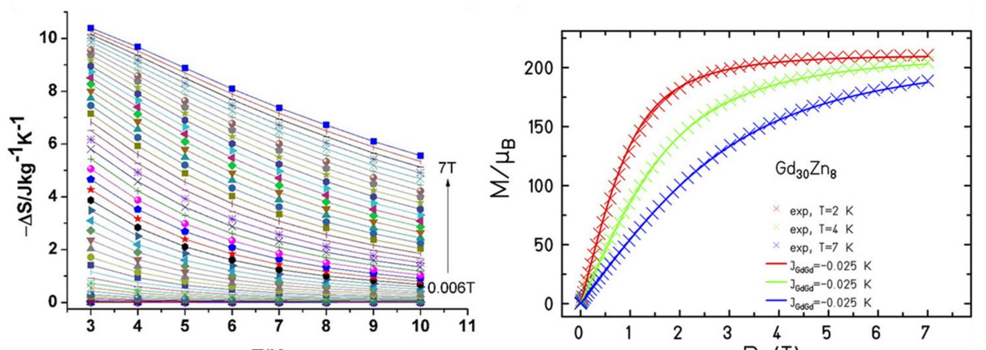
Polyoxometalates (POMs) are usually made up of early transition metals such as tungsten, molybdenum, or vanadium ions in their highest oxidation state and are bridged by oxo ligands. The reactivity of POMs towards transition metals can be tremendously enhanced by creating voids to give "lacunary POMs", where a structural element is missing thereby providing a "super-ligand" system for cationic species such as transition metal ions, or even aggregates of these. Fusion of two different redox and/or photoactive or paramagnetic centers within POM framework can emerge in the form of a new functional materials bearing the robustness of POMs and physical properties two different transition metals. Thus depending on demand, the overall properties of the molecules can be tuned and designed by selecting electronically different metal centers and ligands of different sizes, shapes and charges.[1]



Multifunctional Nanomaterials

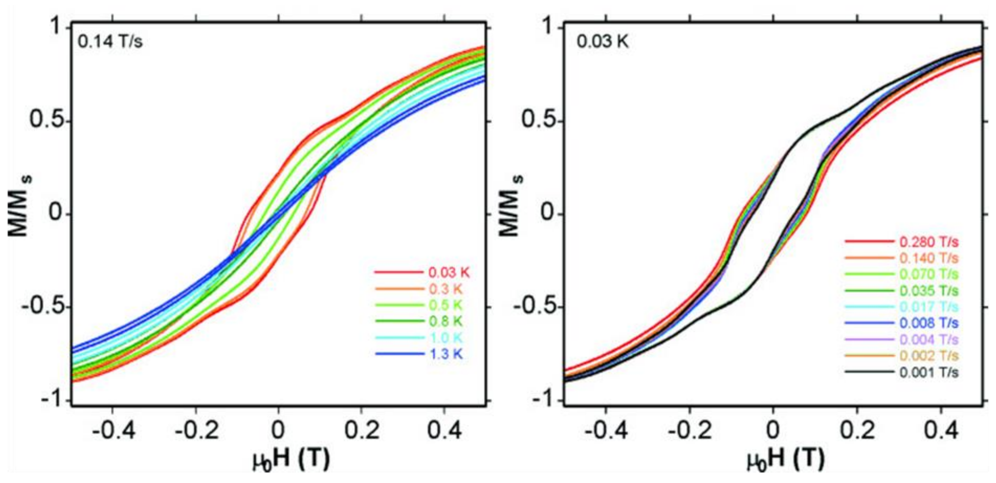
$[Ln_{30}M_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$ **$\{Ln_{30}M_8\}$**
Ln = Gd, Dy or Y, and M = Zn, Mn, Co

Cryogenic Magnetic Cooler

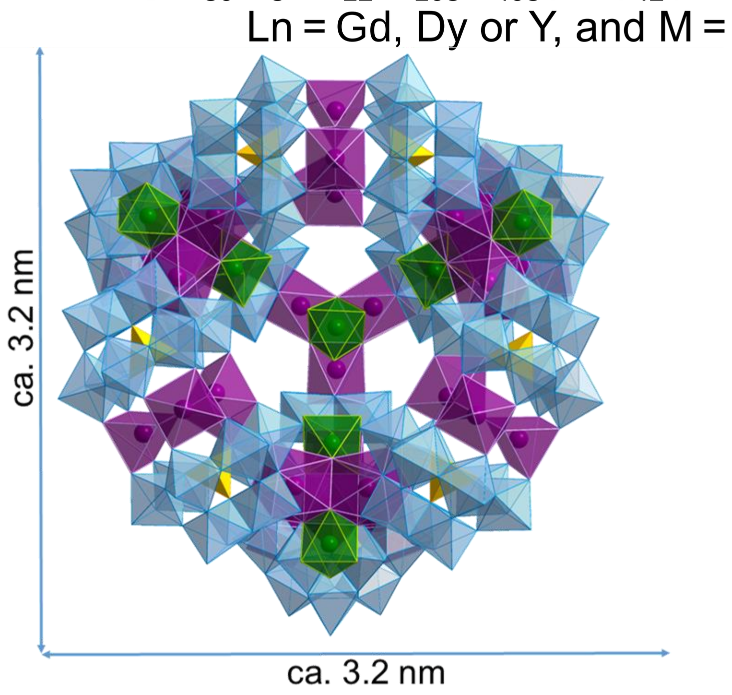


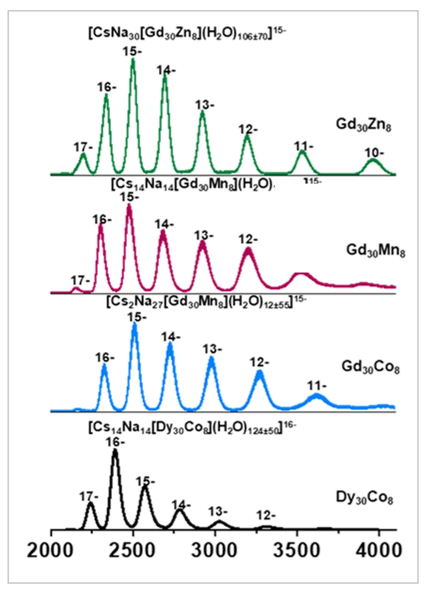
$\{Gd_{30}Zn_8\}$ molecular magnetic cryocoolants.[2]

Single-Molecule Magnet

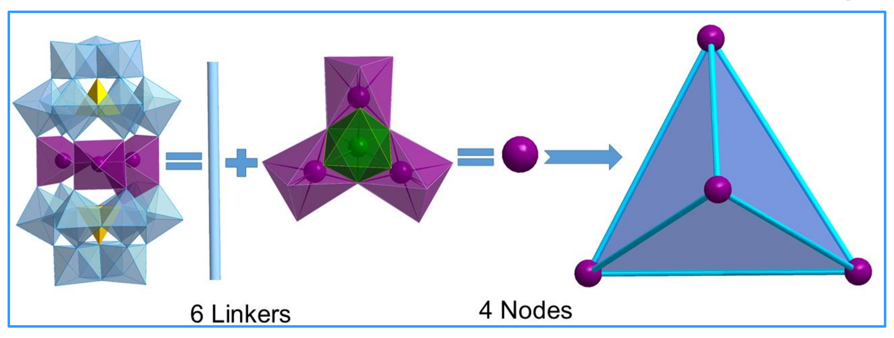


$\{Dy_{30}Co_8\}$ shows single-molecule magnet behavior.[3]

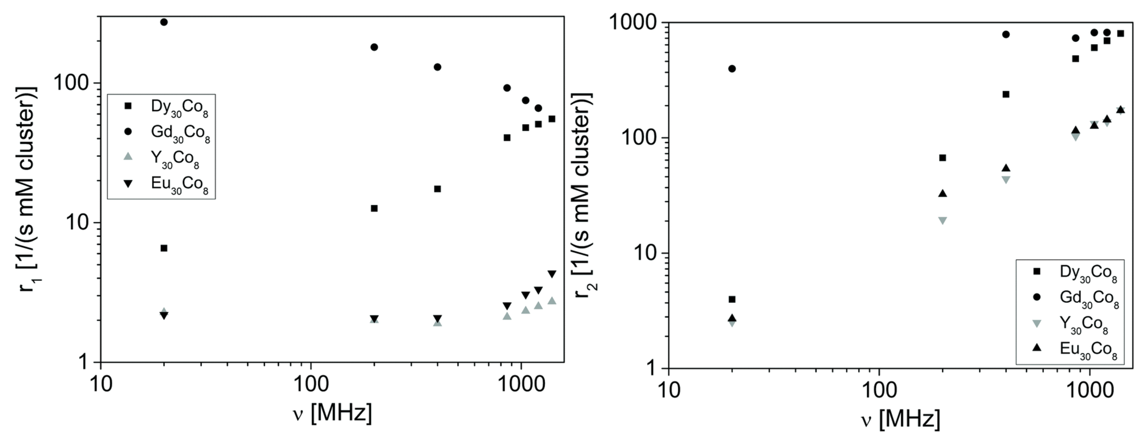


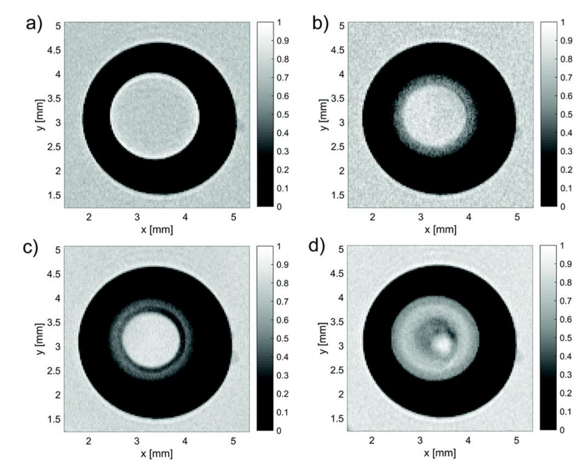


Mass spectrometry data

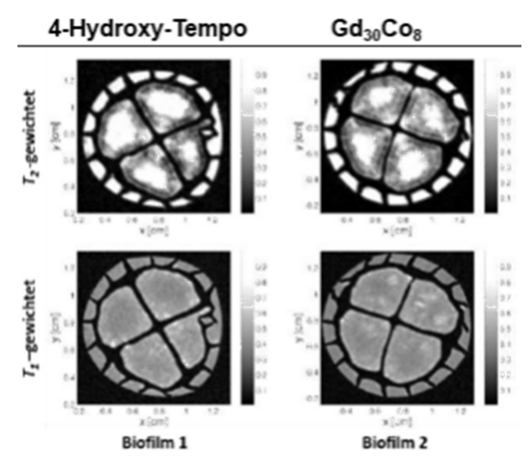


Contrast Agents for High-Field MRI Applications





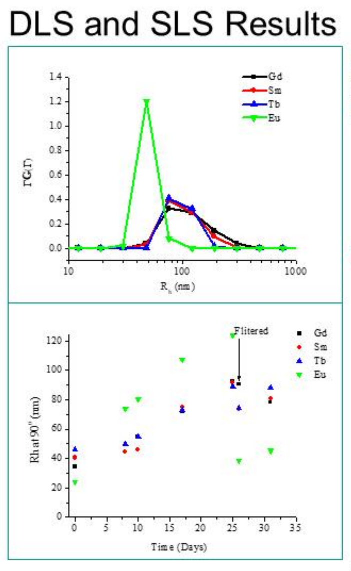
In situ study of deposit layer formation during skimmed milk filtration by MRI.[4]

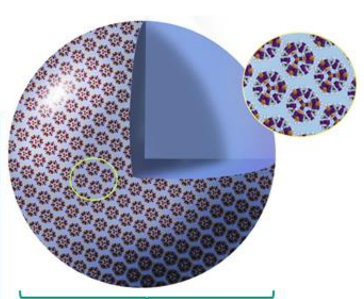


MRI of Biofilm

"Blackberry" Structures

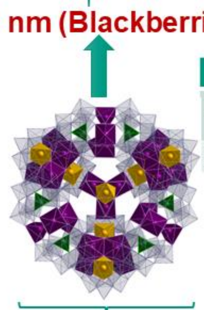
DLS and SLS Results





POMs displays unique solution behavior by self-assembling into single layer, hollow, spherical **"blackberry" structures.**

208 nm (Blackberries)

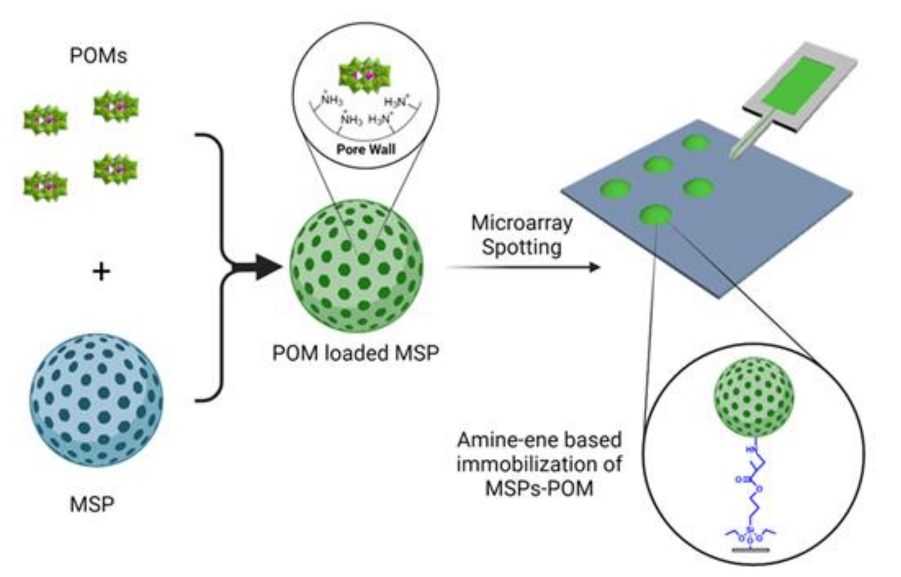


	Sm	Eu	Gd	Tb
$R_{H(0)}$ (nm)	91.9	45.4	103.9	97.0
R_g (nm)	89.4	43.5	105.4	98.1

(R_h) hydrodynamic radius
(R_g) radius of gyration

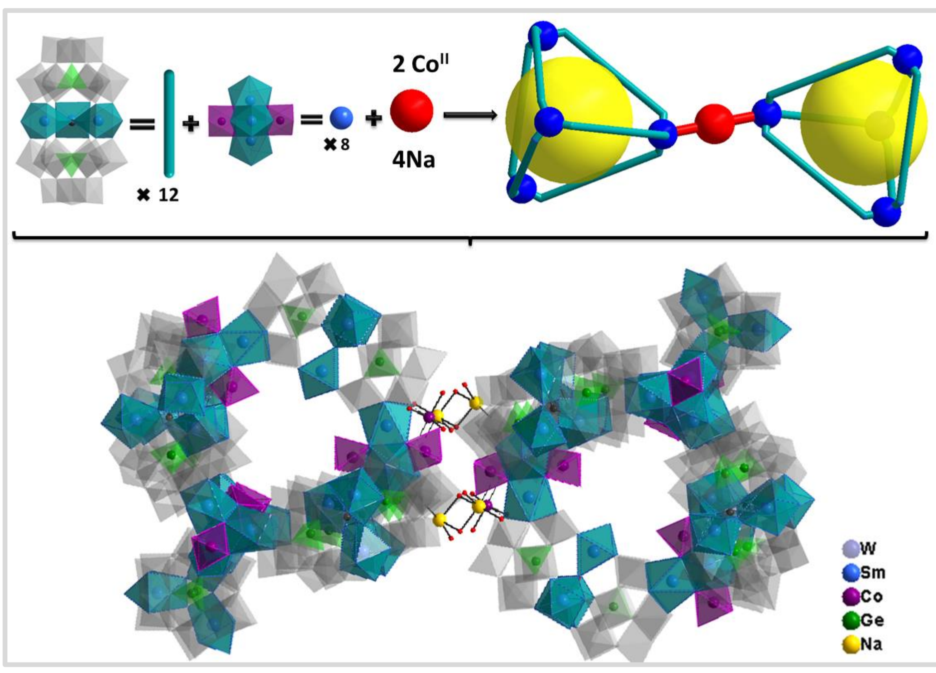
3.2 nm (Discrete Polyanion)

Patterned Immobilization of POM-Loaded MSP

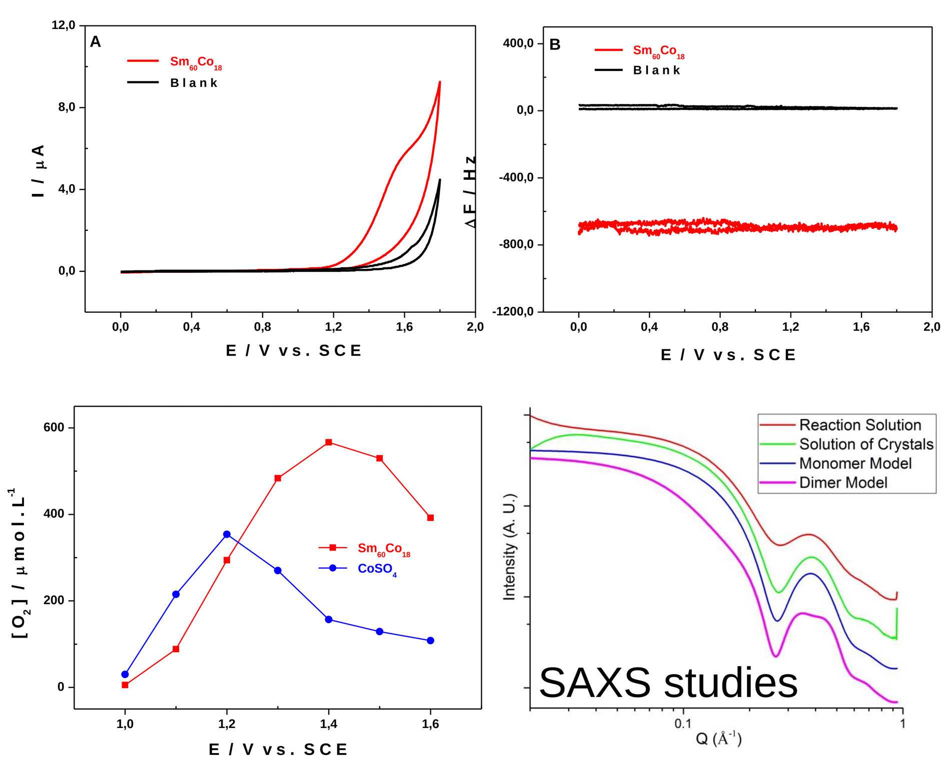


Method to attach POM clusters to mesoporous silica particles for creating functional POM arrays for biomedical sensing and catalysis.

Molecular Catalyst for Water Oxidation

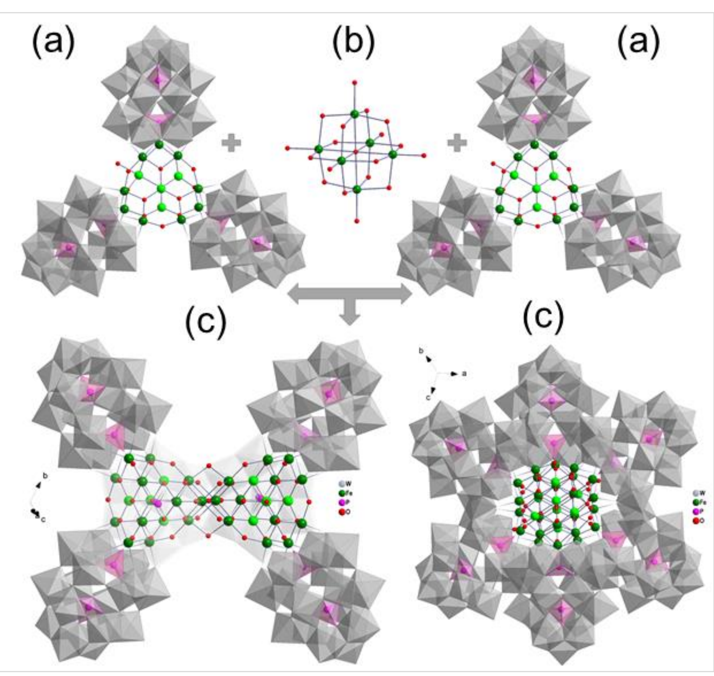


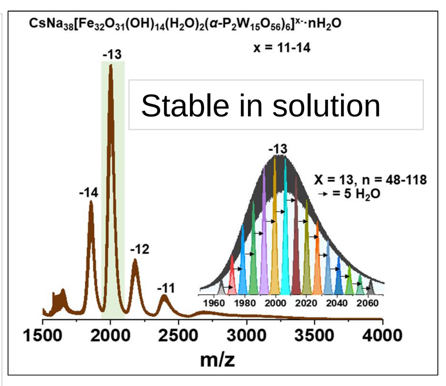
$[\{(GeW_9O_{34})_2Sm_3CO_3(OH_2)_3\}_{12}\{Co_2Sm_3(OH)_6(OH_2)_6\}_8(Co(OH_2)_2)]^{96-}$ **$\{Sm_{60}Co_{18}\}$**



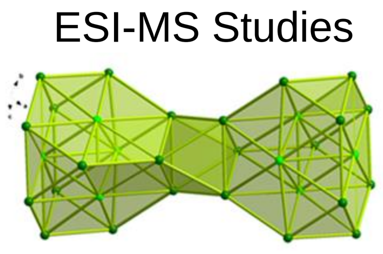
Molecular Mineral Structure

$[Fe_{32}O_{31}(OH)_{14}(H_2O)_2(P_2W_{15}O_{56})_6]^{52-}$ **$\{Fe_{32}\}$**





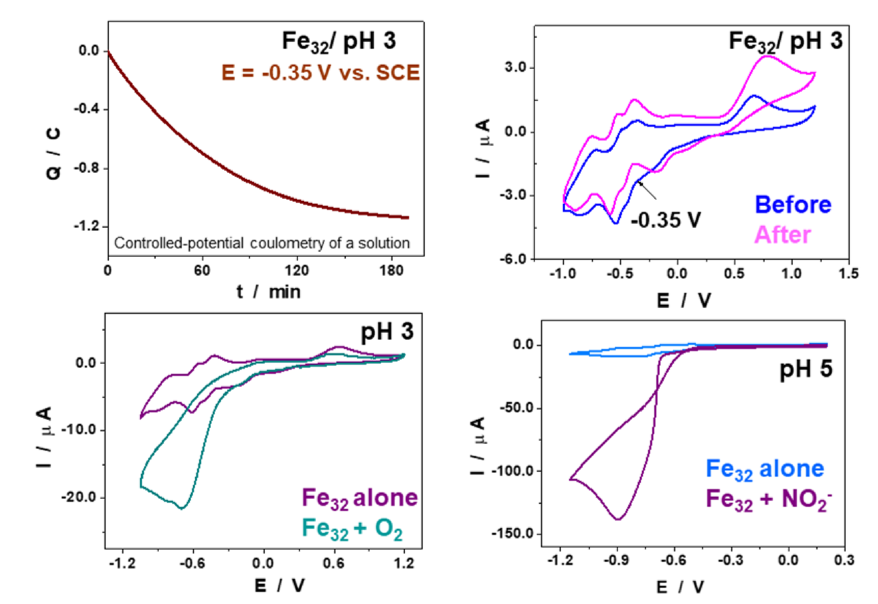
ESI-MS Studies



$\{Fe_{32}\}$ Core

a) $\{Fe_{13}O_{12}(OH)(H_2O)(P_2W_{15}O_{56})_3\}^{22-}$
b) Lindqvist-type polyoxoferrate(III) $\{Fe_6O_7(OH)_{12}\}^{8-}$
c) $[Fe_{32}O_{31}(OH)_{14}(H_2O)_2(P_2W_{15}O_{56})_6]^{52-}$ (Different axis views)

Electro-Catalytic Reduction of Dioxygen and Nitrite ion



[1] A. V. Anyushin, A. Kondinski, T. N. Parac-Vogt, *Chem. Soc. Rev*. **2020**, *49*, 382– 432. [2] M. Ibrahim, Y. Peng, E. Moreno-Pineda, C. E. Anson, J. Schnack, A. K. Powell, *Small Structures* **2021**, *2*, 2100052. [3] M. Ibrahim, V. Mereacre, N. Leblanc, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem. Int. Ed*. **2015**, *54*, 15574– 15578. [4] M. Ibrahim, S. Krämer, N. Schork, G. Guthausen, *Dalton Trans*. **2019**, 48, 15597– 15604. [5] M. P. Merkel, C. E. Anson, G. E. Kostakis, A. K. Powell, *Cryst. Growth Des*. **2021**, *21*, 6, 3179–3190.